PROCESSES CONTROLLING TRACE METAL AND NUTRIENT GEOCHEMISTRY IN TWO SOUTHEAST ALASKAN FJORDS

A

THESIS

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By

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Abstract

Environmental processes controlling trace metal and nutrient chemistry in sediment were investigated in Smeaton Bay and Boca de Quadra, two southeast Alaskan fjords. These pristine, non-glacial fjords (55°20'N) are located in a rugged mountainous region just north of the Alaska-British Columbia border. Close interval sampling and the remote location of the study allowed detailed examination of biogeochemical cycles in an unperturbed system. To do this, for a period of three years, spatial and temporal variations in watershed inputs, marine primary productivity, and sediment geochemistry were examined.

Unlike temperate estuaries where the rivers are often significant sources of nutrients and trace metals, in the Wilson and Blossom Rivers (which drain into Smeaton Bay), the concentrations and export rates of nutrients and copper are low for most of the year. The maximum nutrient export from the Wilson-Blossom system appears to be closely tied to the annual salmon cycle. Iron and manganese export rates from the watersheds are much higher than those for copper, reflecting solubilization of iron and manganese under reducing conditions that develop in muskeg ponds during drought periods. The association of metals with organics allows transport of iron and possibly other metals throughout the fjord system, in contrast with the large-scale removal of metals in or near the river's mouth, observed elsewhere.

Episodic physical mixing and the supply of reactive (autochthonous) organic matter are responsible for the temporal variations observed in interstitial water profiles. In the shallower areas of the fjords, non-linear log ^{210}Pb profiles and enhanced ^{137}Cs penetration depths suggest a substantial terrestrial contribution of sediment, and mixing coefficients ranging from >6.6 to >65 cm^2yr^{-1}. Small scale variability is considerable and interstitial waters are greatly undersaturated with respect to manganese- and iron- phosphates or carbonates. In the deep basin locations, sediment focusing and less mixing result in linear log ^{210}Pb distributions with apparent accumulation rates of 88 $\pm$ 15 mg $cm^{-2}yr^{-1}$, and reducing conditions near the sediment-water interface.

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Preface

SPAWNING

Sleep no longer erases
the creases
that ripple my forehead
like waves on log strewn shores.
Dreams and salmon carcasses
held together by watertight skin
hang on windfalls like discarded gloves,
    their eyes hollow,
    their flesh consumed
    by ravens and gulls.
You, I, and thousands of pinks
return to Smeaton Bay
and swim upstream.
No longer hungry,
our tongues are lost in the recesses
of pleasure swallowed too easily.
Our bloated bodies fight fatigue
and the current that divides us
    into the flight of eagles
    and the fat on bears and seals.
No burial awaits me
in the loose gravel of the Blossom
or Wilson Rivers.
Instead, crumbling
like the poles of Old Kasaan,
moss will grow on my chiseled face,
its roots holding mud
I've scooped from the flooded valley.

Although the 100% cotton rag pages of this dissertation will certainly last longer than the value of the work they describe, I feel this cycle has been closed. Unlike the "humpies" that fertilize the streams of my study area after two years at sea, I've been "at sea" for 15 years, feeding upon the knowledge, experience, and friendship of many people. I am grateful to all of them.

I would like to express my appreciation to the members of my graduate advisory committee, who both individually and collectively insured successful completion of my graduate studies. Dr. David

Burrell, my committee chairman, gave me almost unrestricted freedom to pursue my research interests, and through countless discussions with him, the scope of my thesis expanded far beyond trace metal chemistry. He endured my compulsion with respect to work and athletics, while respecting both my scientific and philosophic opinions. Dr. Dan Hawkins provided encouragement and practical advice during difficult periods of my graduate career, and through his enthusiasm and example made teaching, research, and fun, fully compatible. Dr. Robert Barsdate tutored me for many hours in the art of responding to oral questions, and was instrumental in my passing the PhD comprehensive exam. Dr. George Kipphut provided me with a sounding board for undistilled theories, a discerning eye for overlooked details of global importance, and fresh coffee when I was late staggering into work. Dr. Vera Alexander gave me valuable insight on nutrient cycling and many comments that improved the readability of this thesis. Dr. Joe Niebauer taught me much about estuarine dynamics, and Dr. Walt Johnson guided me through the murky worlds of micro-computers and post-defense hangovers.

My field work involved 20 cruises to Boca de Quadra and Smeaton Bay and my co-workers (the "Boca Mafia," as Dave Shaw dubbed us) deserve special recognition. Frank Flynn, who served as chief scientist through the first two and a half years of the the project, was instrumental in making operations go smoothly and efficiently while accomodating demands that meant the difference between just collecting data and examining scientific questions. John Smithhisler and Page Else were my main assistants during river and watershed

sampling. Donna Weihs, Barry Hogarty, Terri Paluszkiewicz, Norma Haubenstock, Steve Whalen, Carol Winiecki, Bill Kopplin, and others shared the experiences and responsibilities of *M/V Redoubt* cruises, and all contributed to my research in some way.

My studies at the Institute of Marine Science benefitted from the availability of excellent laboratory facilities as well as faculty, students, and staff with whom I could interact. The geochemistry group (which over the years included Jeff Cornwell, Sue Banahan, George Kipphut, Dick Stolzberg, Marc Alperin, Bill Reeburgh, Dave Glover, Susan Henrichs, Gi Hong, Allen Doyle, Carl Johnston, and others) enhanced my research by exposure to new ideas and different perspectives. Marc Alperin, Jeff Cornwell, Steve Whalen, and Carol Winiecki provided essential discussion and criticism. Laurel Hites ably dealt with my departmental paperwork. Dr. Bill Reeburgh gave me access to his laboratory's word processor, and Helen Stockholm and her Publications staff (especially Mauricette Nicpon) assisted in producing the manuscripts from which this dissertation is taken.

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Union/American Society of Limnology and Oceanography Meetings in San Francisco.

Finally, I thank my family and friends for their encouragement and support. I'm especially grateful to my parents, Suteo Francis and Bessie M. Sugai for their patience and understanding.

1. Introduction

The importance of estuarine environments as sources and sinks of river-derived trace metals has been well-documented. Reactions within the freshwater-seawater mixing zone and at the sediment-seawater interface can dramatically alter the flux of dissolved metals reaching the open ocean. Laboratory and field studies have been used to investigate the mixing of river and seawater end-members in estuaries with often conflicting results (e.g. Sholkovitz et al., 1978; Moore et al., 1979; Boyle et al., 1982). It is generally found that the estuarine behavior of Mn, Fe, and Cu is non-conservative (Boyle et al., 1974) and numerous processes are responsible for the observed trace metal distributions. Metals may be removed from estuarine waters by flocculation and sedimentation of dissolved metals in association with colloidal humic acids and hydrous iron oxides (Sholkovitz, 1978). The estuarine metal flux can be increased by release of metals from particulates in the mixing zone (Wilke and Dayal, 1982; Windom et al., 1983) or from estuarine sediments (Evans et al., 1977; Trefry and Presley, 1982).

Long term studies necessary for discerning the interactions between natural biological and geochemical cycles have been conducted almost exclusively in shallow, coastal environments, where man's impact is a major component of the existing chemical mass balances. In many of these shallow environments, benthic processes are occurring within the euphotic zone, further complicating the sediment processes. This thesis addresses the relative importance of trace metal and

nutrient fluxes from the watersheds and sediments of Smeaton Bay and Boca de Quadra, two fjords located in a rugged mountainous region just north of the Alaska-British Columbia border. At the time this study was undertaken, the drainage network and fjord waters of these systems were pristine, allowing study of the existing biotic regulation of hydrological and biogeochemical parameters. Although this provided some analytical and sampling problems, the opportunity to examine a natural fjord over several years outweighed the difficulties.

Fjords are important features on the western coast of North America at latitudes greater than 45°N. Geologically recent features, fjords are characterized by steep topography, length much greater than width, and one or more entrance sills restricting water exchange between the sub-euphotic basins and adjoining coastal water. These characteristics will prove important to this study and will be discussed as they apply to processes being examined.

STUDY SITE

Smeaton Bay and Boca de Quadra, two adjacent fjord-estuaries carved within the Coast Range batholith during the Pleistocene glaciation, are characterized by deep, narrow basins with steep walls and sills of glacial origin. Although small active glaciers exist within the high relief watersheds, they do not affect streamflow or freshwater chemistry. However, the steep topography limits the river drainage areas and minimizes the response time of the rivers to events occurring in the watersheds. The natural vegetation is dominated by a dense forest of Sitka spruce (*Picea sitchensis*) and western hemlock

(*Tsuga heterphylla*) with extensive regions of poorly drained muskeg. The region is characterized by cool summers, mild winters, and annual precipitation in excess of 400 cm. Soils are highly leached with low pH and nutrient values.

Although the circulation of most fjord-estuaries is driven by freshwater input within the fjords, Smeaton Bay and Boca de Quadra appear to be driven "backward", or by low salinity water available outside the fjord. Thus, there is subsurface inflow with compensating net outflow over the sill. Nebert and Burrell (1982) suggest that this "backward" flow may result in large part because in Boca de Quadra and Smeaton Bay, the tidal volume is much greater than the river water entering during one tide. The tidal range in these fjords is 2 to 6 m over a fortnightly period, and the tidal volume is that range multiplied by the surface area it is affecting. During periods of high discharge, Boca de Quadra receives freshwater from the Keta and Marten Rivers amounting to only 1.5 to 2% of the tidal volume; Smeaton Bay receives about 4% of the tidal volume from the Wilson-Blossom Rivers under similar conditions because its watershed area is 25.4 times that of the fjord area, whereas the ratio is 10.3 for Boca de Quadra. Thus, the driving force supporting the above-sill circulation is thought to be the brackish water derived from coastal British Columbia.

The deep waters of Smeaton Bay and Boca de Quadra exhibit a strong seasonal pattern: a period of deep water renewal begins in spring and ceases in late summer followed by a period of relative

isolation. The driving force for the deep water renewal is the dense, deep water formed during spring and summer when continental shelf waters enter the adjacent waterways because of the cessation of winter downwelling (Royer, 1975).

STUDY APPROACH AND EVOLUTION

The initial objective of this study was to examine interstitial water profiles from different locations in Smeaton Bay and Boca de Quadra to determine the role of natural organic matter upon trace metal diagenesis in sediments. To do this, I examined the sources of trace metals and organic matter, specifically river input and primary productivity. Chapter 2 examines the transport of dissolved organic carbon, nutrients, and trace metals from the Wilson and Blossom Rivers to Smeaton Bay. The results of the primary productivity study as they affect sediment chemistry will be discussed in Chapter 3. Early results from interstitial water profiles demonstrated temporal and small scale spatial variability in the sediment. These effects could not be attributed to steady-state chemical processes and thus, it became necessary to examine perturbations on time scales short with respect to the residence times of reactive elements. The importance of time scales developed into the detailed geochronology study which appears as Chapter 3. Finally, in Chapter 4, combining the geochronologies with 3-year time and spatial series of interstitial nutrient and trace metal profiles, I estimate the relative importance of physical and chemical processes upon the observed sediment chemistry.

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2. Transport of Dissolved Organic Carbon, Nutrients, and Trace Metals from the Wilson and Blossom Rivers to Smeaton Bay, Southeast Alaska

Abstract- Regional and seasonal differences in chemical input from the Wilson and Blossom rivers, two pristine, major salmon-producing rivers in southeast Alaska, were examined. For a period of 2 yr, riverine concentrations of dissolved organic carbon, nutrients, Cu, Fe, and Mn were determined at approximately monthly intervals and used to calculate export rates. Because of extremely high annual precipitation (400-450 cm) and drainage basins restricted by high topographical relief, the concentrations and export rates of nutrients and Cu in the rivers are low for most of the year. The maximum nutrient export from the Wilson-Blossom system appears to be closely tied to the annual salmon cycle. Iron and Mn export rates from the watersheds are much higher than those for Cu, reflecting solubilization of Fe and Mn under reducing conditions that develop in muskeg ponds during drought periods. The association of metals with organics allows transport of Fe and possibly other metals throughout the fjord system, in contrast with the large-scale removal of metals in or near the river's mouth, observed elsewhere.

INTRODUCTION

The salmon fisheries of southeast Alaska are a resource of enormous commercial, subsistence, and recreational value. However, in the decade ahead, mining and logging developments within the watersheds of natural salmon rivers will present inevitable management

conflicts for fisheries officials. Because the structure of a stream ecosystem is determined by characteristics of its drainage network (Hynes, 1975; Vannote et al., 1980), altered land usage can upset the existing biotic regulation of hydrological and biogeochemical characteristics (Bormann and Likens, 1979). A fluctuating water regime can destabilize streambed composition and geomorphology causing increased erosion and siltation. This reduces the quality of food (Sloane-Richey et al., 1981) and habitat (Naiman and Sedell, 1981) for salmonid fishes. In addition, significant changes in the availability of carbon, nutrients, and trace metals to the stream system could alter the number of salmon migrating to the estuary and beyond.

In 1980 when I began this study I found no literature on the chemistry of any of the over 2000 salmon-producing streams in southeast Alaska. Because increasing development poses an immediate threat to an enormously important fisheries resource, there was a pressing need to determine the biological and chemical cycles present in this environment. A thorough study of a pristine salmon river from a watershed perspective would be valuable to fisheries managers responsible for reestablishing historical salmon runs, enhancing depleted stocks by artificial propagation, and managing natural streams. This study represents a first attempt at quantifying some of the chemical exports occurring in a natural salmon stream. To do this, I examined the annual transport of dissolved organic carbon, nutrients, and trace metals from the Wilson and Blossom rivers.

Because my objective was to examine the transport of dissolved

substances from the Wilson-Blossom river system that were relevant to salmonid habitat, I limited my scope to chemical variables that would yield the most information and serve as models for unmeasured chemical species. Hence, I studied the carbon and nutrient exports to determine possible restraints on productivity, and the trace metals to examine transport mechanisms of potential toxicants. Copper was selected for detailed examination because although it is utilized by phytoplankton as a micronutrient, at elevated concentrations several soluble Cu species are toxic to microfauna and higher organisms including fish (e.g. Whitfield and Lewis, 1976; Lorz and McPherson, 1976; Chakoumakos et al., 1979). Iron and Mn were also chosen for study because of their involvement in redox-coupled reactions and because hydrated ferric oxides and manganese dioxides can be important scavenging agents for heavy metals (Lion et al., 1982; Olsen et al., 1982).

STUDY AREA

The Wilson-Blossom river system (55° 24.8'N, 130° 36.4'W) is located in a rugged mountainous region approximately 28 km northeast of Ketchikan, Alaska (Fig. 1). The high relief limits the river drainage area and minimizes the response time of the river to events occurring in the watershed. The natural vegetation is dominated by a dense forest of Sitka spruce (*Picea sitchensis*) and western hemlock (*Tsuga heterphylla*) with extensive regions of poorly drained muskeg. The region is characterized by cool summers, mild winters, and heavy precipitation. Normal annual precipitation is 400-450 cm (USDA Forest Service, 1979), with October and November usually the wettest months.

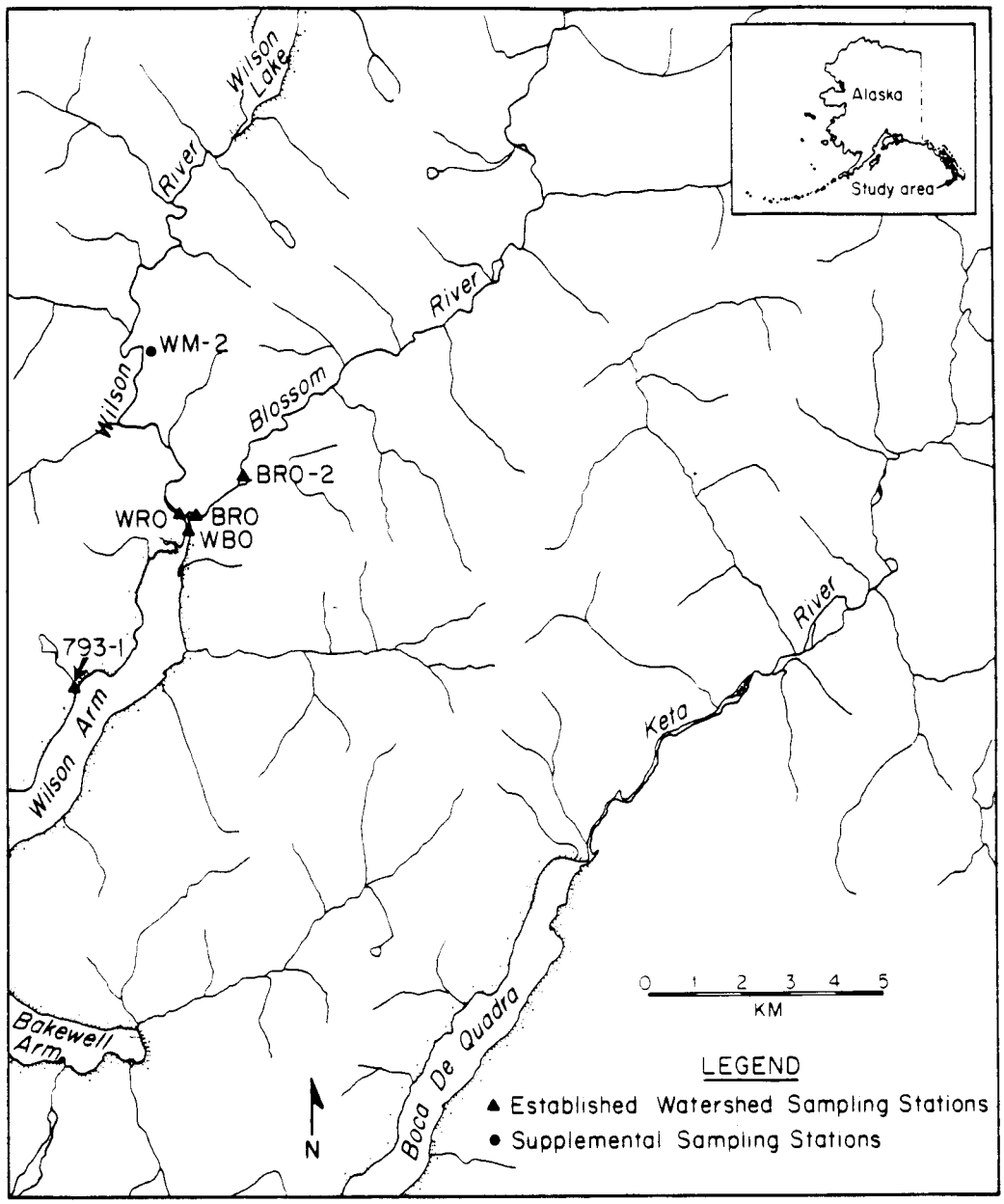


Fig. 1. Location of study sites on the Wilson-Blossom River and in watershed of Smeaton Bay.

At sea level most precipitation is in the form of rain although at higher elevations snow accumulates between December and April. The Wilson and Blossom rivers meet about 0.8 km from Wilson Arm at the head of Smeaton Bay (Fig. 2), a steep-walled, glacially formed fjord. Physical and chemical characteristics of the rivers are given in Table 1. Both the Wilson and Blossom rivers experience spring freshets in May-June when accumulated snow begins melting at higher elevations and strong autumn freshets (September-November) during the rainy season (Fig. 3). Flows during winter (December-April) and late summer (August) are generally low except during occasional storms.

The Wilson-Blossom river system is a natural salmon stream system. Four of five North American species of Pacific salmon are commonly found in the Wilson and Blossom rivers; only sockeye salmon (*Oncorhynchus nerka*) is rare. Pink or humpback salmon (*O. gorbuscha*) is the numerically dominant and commercially most important species, followed by chum or dog salmon (*O. keta*), coho or silver salmon (*O. kisutch*), and chinook or king salmon (*O. tshawytscha*).

MATERIALS AND METHODS

Sampling Methods

From June 1980 to August 1982, stations on the Wilson Blossom rivers and at selected sites in the watershed of Smeaton Bay (Fig. 1) were sampled at approximately monthly intervals for dissolved organic carbon (DOC) and dissolved nutrients; samples for Cu, Fe, and Mn were routinely collected beginning March 1981.

To minimize the effects of tidal variations in trace elements

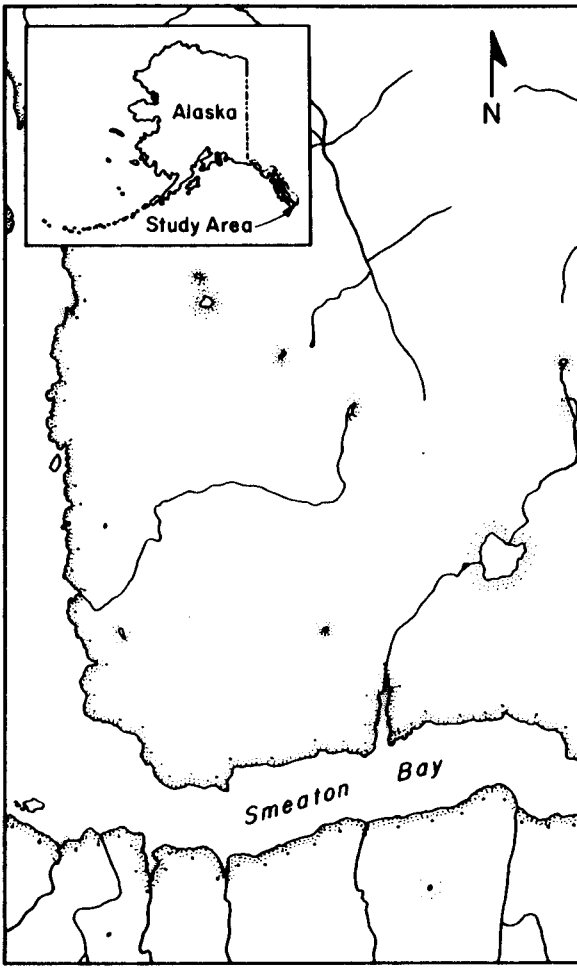


Fig. 2. Location of stations in Smeaton Bay.

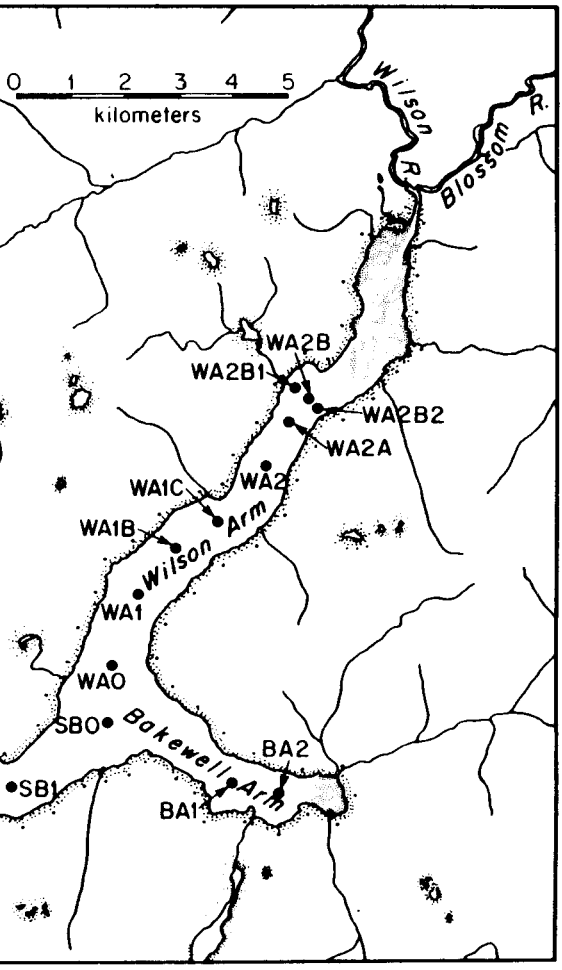

0 1 2 3 4 5
kilometers
Wilson R.
Blossom R.
WA2B
WA2B1
WA2B2
WA2A
WA2
WA1C
WA1B
Wilson Arm
WA1
WA0
SB0
Bakewell Arm
BA2
SB1
BA1

Table 1. Physical and chemical characterization of rivers.

Parameter	WRO Wilson River	BRO Blossom River
Stream order[a]	3	3
Links[b]	26	20
Watershed area (km^2)	294	181
Mean annual discharge ($m^3\ s^{-1}$)	33.0[c]	20.2[c]
Gradient (%)	1.45	2.52
Proportion of basin above tree line (%)	42	51
pH (June 3, 1982)	5.8	6.9

[a] Strahler (1957)

[b] Shreve (1966)

[c] U.S.D.A., National Forest Service (1982)

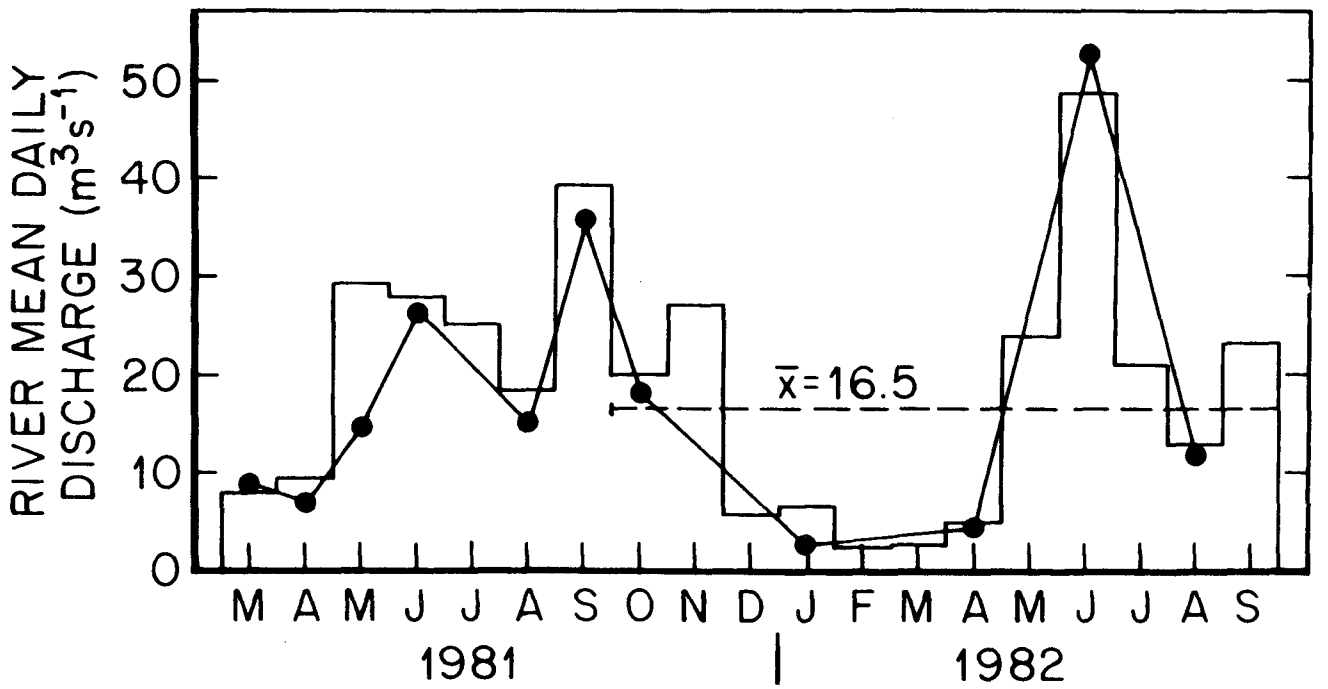


Fig. 3. Blossom River mean daily discharge. Histogram shows monthly mean value for daily discharge. Points show mean daily discharge on sampling dates.

(Boyden et al., 1979), I sampled the rivers within 2 h of high tide. Unfiltered samples were collected approximately 0.5 m below the surface in an upstream direrion as far as possible away from the shore and skiff.

Early results demonstrated the need for extreme caution against contamination in DOC and trace metal samples. Because of the potential for contamination, most of the trace metal samples were collected unfiltered. I adopt the convention of Boyle et al., (1977b) and report metal concentrations as "acid soluble," or those metals in the sample that are converted to a labile form by acidification to less than pH 2. River trace metal samples were collected directly into linear polyethylene (LPE) sample bottles that had been acid cleaned for 1 wk with 6 mol $HCl \cdot L^{-1}$, soaked with quartz double-distilled water (Q water) for several weeks during which the rinse water was changed at least four times, and dried at room temperature in a laminar flow hood (Environmental Air Control, Inc.) in a clean room. Acid-washed LPE sample bottles were opened below the water surface (to avoid contamination from the surface film), rinsed three times, filled approximately two-thirds full, acidified with Ultrex HCl (Baker Chemical Co.), and stored frozen until analysis.

River water samples for dissolved Cu and DOC were collected from below the surface with an acid-cleaned, 20-mL all-glass syringe. Two syringe volumes (40 mL) of river water were forced through the syringe and discarded. The third syringe volume (20 mL) was forced through two combusted Whatman EPM 1000 glass fiber filters preloaded in a 25-mm diameter, acid-cleaned polypropylene Swinnex filter holder

(Millipore Corp.). Use of two filters allowed using the Swinnex holder without the supplied silicone gasket, which was found to be a source of metal contamination. After discarding the first 20 mL of river water that was filtered, the next 40 mL was collected for Cu analyses in an acid-cleaned, 60-mL LPE bottled, acidified with Ultrex HCl, and stored frozed. Samples for DOC were filtered directly into precombusted 20-mL glass ampules, immediately heat sealed and refrigerated in darkness prior to processing. As a precaution against overloading the filters, no more than 60 mL was filtered through a filter set, and if visual inspection indicated substantial particulate material accumulating on the filter (the Swinnex holders are transparent), a new filter set was used. Samples for inorganic nutrient analyses were filtered through a 0.45-um Millipore filter and frozen for subsequent analysis.

Analytical Methods

DOC and POC samples were sealed into 10-mL precombusted ampules on board ship along with 0.1 g of $K_2S_2O_8$ and 0.25 mL of 6% H_3PO_4 using a modification of the persulfate oxidation method of Strickland and Parsons (1972). To minimize procedural blanks of 0.2 - 0.5 mg $C \cdot L^{-1}$, I made a series of three standard additions of dextrose in duplicate or triplicate to each DOC sample and a linear regression made for the 10 points obtained. For POC samples, at each station four replicates were filtered through pre-ashed Gelman glass fiber filters and sealed with $K_2S_2O_8$, H_3PO_4, and 5 mL of Q water added with a glass repipette. Samples were compared with dextrose standards added to ampules

containing a preashed filter and the other reagents.

Dissolved inorganic and total nutrients were determined by auto-analyzer. For ammonia, the method used was that of Koroleff (1970). Nitrite was determined by the Greiss reaction, as described by Armstrong et al. (1967). Nitrate is quantitatively reduced to nitrite using copperized Cd filings. The inorganic phosphate procedure used was that of Murphy and Riley (1962).

Iron was analyzed using the ferrozine technique of Stookey (1970), as applied to natural waters by Murray and Gill (1978) and Gibbs (1979). Copper and Mn determinations were made using a Perkin-Elmer model 360 atomic absorption spectrophotometer and a HGA 2100 graphite furnace. At least three injections of each sample were made. The relative standard deviation for Mn using 25-uL injections was consistently less than 5% for samples between 0.8 and 8 $ug \cdot L^{-1}$. The relative standard deviation for Cu using one or two 50-uL injections was approximately 15% or less for concentrations in the range of 0.5 $ug \cdot L^{-1}$ or less.

Daily discharge by the Blossom River was gauged by the U.S. Geological Survey at a station established on February 11, 1981, at 55° 25.34'N, 130° 33.40'E, roughly 1.5 km upstream from station BRO-2 (Fig. 1). To obtain discharge values for the Wilson River, I used computed synthetic-flow data (L. Bartos, USDA Forest Service, Ketchikan, AK, personal communication) for both the Wilson and Blossom rivers to adjust measured 1981-1982 Blossom River flow data for the Wilson River. The synthetic flow data were generated from input of precipitation, drainage area, proportion of basin above tree line,

proportion of basin in main channel lakes, slope of main channel, mean elevation of basin, and south distance to Dixon entrance.

To calculate the monthly chemical inputs of the Wilson and Blossom rivers I used the monthly mean daily discharge and measured concentrations. The mean daily discharge of the Blossom River on the actual sampling dates (solid circles) versus the monthly mean (histogram) is shown in Fig. 3. Because of the close agreement between the flow measured on the sampling date and the monthly mean (R^2=0.91) I feel that my sampling does not reflect anomalous dates within a given month. For months in which no actual samples were collected, I used a mean between the month preceding and following.

RESULTS

DOC and POC Concentrations and Total DOC Export

The DOC concentrations of the Wilson and Blossom rivers exhibit seasonal variations but the annual range is <3 mg $C \cdot L^{-1}$ (Fig. 4a). The Wilson River generally has higher DOC concentrations (mean 4.0 $\pm$ 1.1 mg $C \cdot L^{-1}$) than the Blossom River (mean 2.5 $\pm$ 0.7 mg $C \cdot L^{-1}$).

The POC concentrations in these rivers account for less than 10% of the total carbon. POC values and the DOC:POC ratios for the rivers are shown in Table 2. POC measurements were made in the 1982 field season only and may not represent generalized conditions. The DOC:POC ratios in the Wilson and Blossom rivers were almost identical in April 1982, a low-flow period prior to snowmelt at higher elevations of the watershed. During the high flow period in June, the DOC:POC ratios of the Blossom River (BRO) and the Wilson-Blossom confluence (WBO)

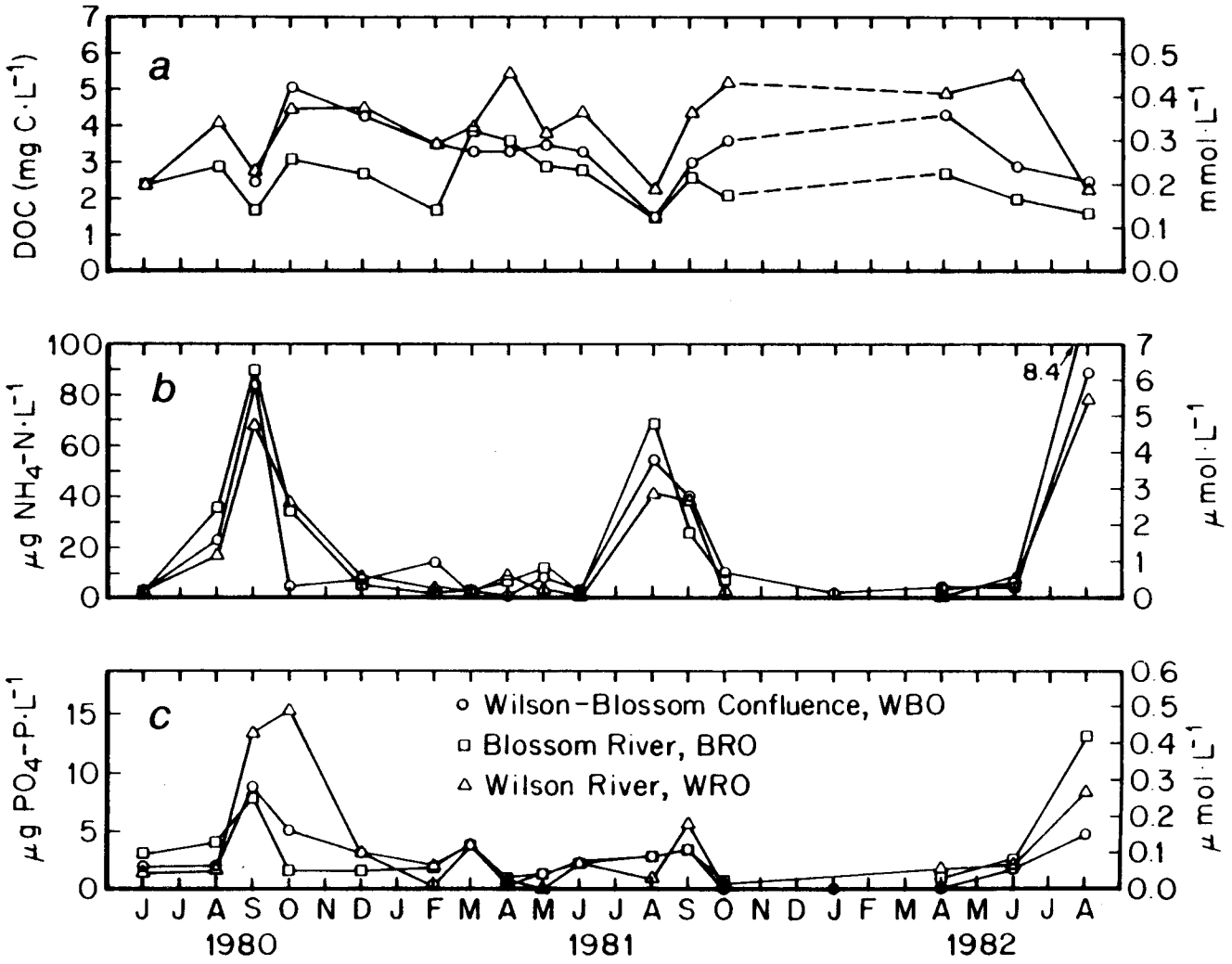


Fig. 4. a. Dissolved organic carbon vs. depth for Wilson-Blossom confluence, Blossom River, and Wilson River.
b. Dissolved ammonia vs. time.
c. Dissolved inorganic phosphate vs. time.

Table 2. POC values and DOC:POC ratios for river stations, 1982.

Station	Location	April POC[a] mgC·L^{-1}	April DOC:POC	June POC mgC·L^{-1}	June DOC:POC	August POC mgC·L^{-1}	August DOC:POC
WBO	Wilson-Blossom confluence	0.14±0.01	30.7	0.18±0.03	15.9	0.16±0.01	15.6
WRO	Wilson River	0.22±0.02	22.6	0.15±0.02	36.3	0.19±0.01	12.1
BRO	Blossom River	0.12±0.01	21.4	0.21±0.02	9.8	0.15±0.01	10.4
BRO-2	Blossom River, upstream	-		0.16±0.01	16.7	0.15±0.02	10.9

[a]Mean of 4 determinations ± 1 standard deviation.

decrease, while the ratio for the Wilson River (WRO) increases. In August, another low-flow month, the river DOC:POC ratios are either lower than June (for station WRO) or nearly the same (BRO and WBO).

The transport of DOC from the rivers to the fjord is bimodal, with 30% of the annual Blossom River DOC export (Table 3) occurring in May and June and 37% in September-November. For the Wilson River (Table 4) 22% of the annual export occurs in May and June and 44% in the three autumn months. Thus, for the year between March 1981 and February 1982, the Wilson River contributed 3.25×10^{8} mol of DOC, while the Blossom River exported 1.19×10^{8} mol. As shown in Table 5 the annual DOC export per unit area of watershed for the Wilson River (13.3 g $C \cdot m^{-2} yr^{-1}$) is greater than for the Blossom River (7.9 g $C \cdot m^{-2} yr^{-1}$).

Nitrogen and Phosphorus Concentrations and Annual Exports

There are distinct seasonal variations in dissolved inorganic nitrogen and phosphorus concentrations in the Blossom and Wilson rivers. Ammonia is extremely low (<1 $umol \cdot L^{-1}$) at the three main river stations (Fig. 4b), with peak concentrations of 4-6 $umol \cdot L^{-1}$ occurring late summer-early fall. Phosphate concentrations (Fig. 4c) are near analytical detection limits during most of the year except in late summer-autumn. Nitrate + nitrite has a less noticeable seasonal cycle, with concentrations generally rising through the fall-winter season.

The monthly river export rates for nitrate + nitrite (Table 3) are highest for the Blossom River in September 1981, a period of high

Table 3. Monthly chemical input from the Blossom River into Wilson Arm, March 1981-February 1982.

	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Annual Export
DOC (10^6 mol)	6.7	7.5	18.8	16.6	12.1	5.9	22.3	9.6	12.4	2.7	3.0	1.0	119
NO_3+NO_2 (10^3 mol)	152	199	488	252	232	171	1520	250	476	103	118	38	4000
NH_4 (10^3 mol)	5.3	11.4	59.5	10.8	167	239	178	24.4	23.6	5.1	5.9	1.9	732
PO_4 (10^3 mol)	2.8	0.75	3.1	5.7	5.3	4.4	11.2	1.1	1.4	0.29	0.35	0.12	36.5
Cu (10^3 mol)	0.07	0.06	0.43	0.46	0.37	0.22	0.69	0.26	0.36	0.08	0.09	0.03	3.12
Fe (10^3 mol)	34	54	213	117	131	113	394	89	142	31	35	11	1360
Mn (10^3 mol)	1.8	2.6	7.3	4.7	6.1	5.7	18.1	5.2	7.4	1.6	1.8	0.6	62.9

Table 4. Monthly chemical input from the Wilson River into Wilson Arm, March 1981-February 1982.

	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Annual Export
DOC (10^6 mol)	12.3	19.7	36.7	39.6	26.8	14.7	60.6	37.8	47.1	11.5	13.9	4.0	325
NO_3+NO_2 (10^3 mol)	130	169	464	31	88	120	505	191	505	123	148	43	2520
NH_4 (10^3 mol)	7.5	24.9	28.7	12.8	276	212	239	17.6	18.4	4.4	5.4	1.6	848
PO_4 (10^3 mol)	4.5	0.86	0.0	7.5	4.8	2.3	29.5	0.0	2.4	0.56	0.67	0.19	53.3
Cu (10^3 mol)	0.18	0.09	0.60	0.33	0.36	0.34	0.85	0.62	0.67	0.16	0.20	0.06	4.46
Fe (10^3 mol)	74	117	330	121	110	89	370	183	247	60	73	21	1800
Mn (10^3 mol)	2.9	3.8	10.2	5.5	5.1	4.3	8.6	6.9	8.6	2.1	2.5	0.7	61.2

mean daily discharge. Likewise, for the Wilson River (Table 4) the highest nitrate + nitrite export rates (September and November 1981) correspond with peak discharge rates. However, for ammonia the export increases in both rivers prior to the high-flow times. The maximum phosphate export from the Wilson and Blossom rivers occurs in September. The annual nutrient exports per unit watershed area are tabulated for the Wilson and Blossom rivers in Table 5.

Annual Concentrations and Exports of Cu, Fe, and Mn

Because of highly leached soils and high discharge rates, the concentrations of acid-soluble Cu are extremely low (less than 0.7 $ug \cdot L^{-1}$ or 11 $nmol \cdot L^{-1}$) (Fig. 5). Based on a limited number of samples (Fig. 5b) the particulate Cu phase appears to be more important for Blossom River than for the Wilson River. However, because of the extremely low levels of acid-soluble Cu, it is difficult to discern spatial differences.

The seasonal export of Cu reflects the small concentration range for the metal and its apparent dependence on flow. For the Blossom River, 40% of the annual transport occurs during May-July and an additional 22% is removed in September (Table 3). In the Wilson River, the export of Cu initially peaks in May, decreases somewhat during June-August, then increases dramatically in September and remains high through November. During the autumn period 48% of the annual Cu load of the Wilson River is carried to Smeaton Bay (Table 4). As shown in Table 5, the annual acid-soluble Cu exports per unit area for the Blossom and Wilson watersheds for the year March 1981-February 1982 are virtually identical (1.1 mg $Cu \cdot m^{-2} yr^{-1}$ for the

Table 5. Annual chemical export per unit area for watersheds, March 1981-February 1982.

		Blossom River This study	Wilson River This study	Nanaimo River (Naiman and Sibert, 1978)
DOC	mol m^{-2} yr^{-1}	0.66	1.1	
	g C m^{-2} yr^{-1}	7.9	13.3	14.5
NO_3+NO_2	mmol m^{-2} yr^{-1}	22	8.6	
	mg NO_3-N m^{-2} yr^{-1}	310	120	73
NH_4	mmol m^{-2} yr^{-1}	4.0	2.9	
	mg NH_4-N m^{-2} yr^{-1}	57	40	190
PO_4	mmol m^{-2} yr^{-1}	0.20	0.18	
	mg PO_4-P m^{-2} yr^{-1}	6.2	5.6	
Cu	mmol m^{-2} yr^{-1}	0.017	0.015	
	mg Cu m^{-2} yr^{-1}	1.1	0.96	
Fe	mmol m^{-2} yr^{-1}	7.5	6.1	
	g Fe m^{-2} yr^{-1}	0.42	0.34	
Mn	mmol m^{-2} yr^{-1}	0.35	0.21	
	mg Mn m^{-2} yr^{-1}	19	11	

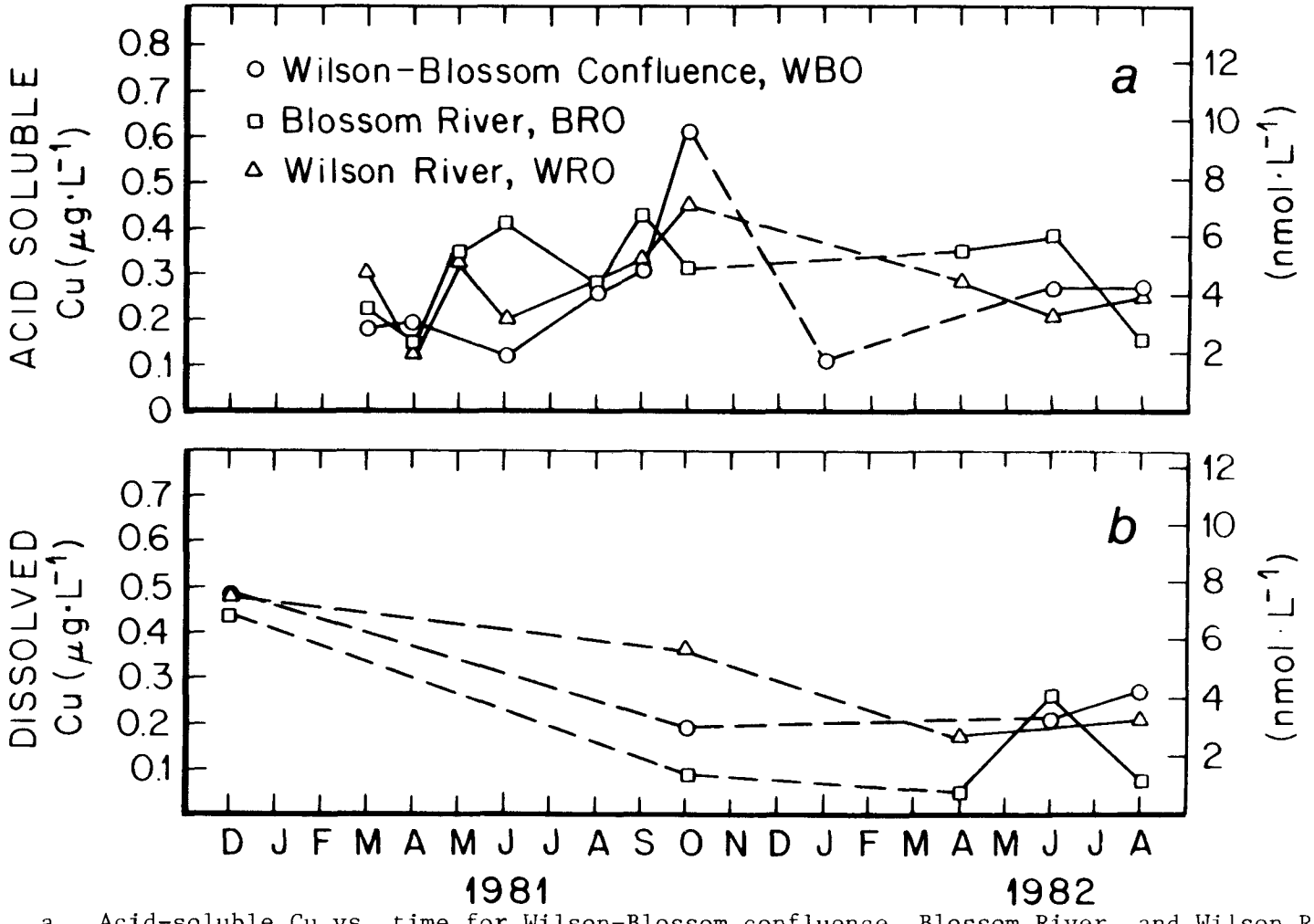


Fig. 5. a. Acid-soluble Cu vs. time for Wilson-Blossom confluence, Blossom River, and Wilson River.
b. Dissolved Cu vs. time.

Blossom River and 0.96 mg Cu· m^{-2} yr^{-1} for the Wilson River). In addition, if data primarily from the 1982 field season are used to calculate annual export rates (September 1981-August 1982), the results are unchanged. For the latter period the Cu export rate for the Blossom River is 1.1 mg Cu·m^{-2} yr^{-1} and for the Wilson River is 0.91 mg Cu·m^{-2} yr^{-1}.

The curves of acid-soluble Fe (Fig. 6a) and acid-soluble Mn (Fig. 6b) versus time are very similar. The dominant peak in concentration for both Fe and Mn occurs in September-October when the autumn rains flush the watershed.

The export rates of acid-soluble Fe from the Blossom and Wilson rivers have sharp peaks in May and September, reflecting the seasonal peaks in concentration as well as flow. Sixteen percent of the Blossom River export of Fe occurs in May and 29% in September. In the Wilson River, the Fe transport rate can be grouped as follows: 18% in May and 44% between September and November. The annual Fe export for the Blossom River is 0.42 g Fe·m^{-2} yr^{-1} and for the Wilson River is 0.34 g Fe·m^{-2} yr^{-1}.

The Mn export from the Blossom River is greatest in September (29%). For the Wilson River 17% of the Mn export occurs in May, 14% in September, and 14% in November. However, the export rates remain relatively high throughout the summer and fall for both rivers. The annual Mn export rate for March 1981 - February 1982 is 19 mg Mn·m^{-2} yr^{-1} for the Blossom River and 11 mg Mn·m^{-2} yr^{-1} for the Wilson River.

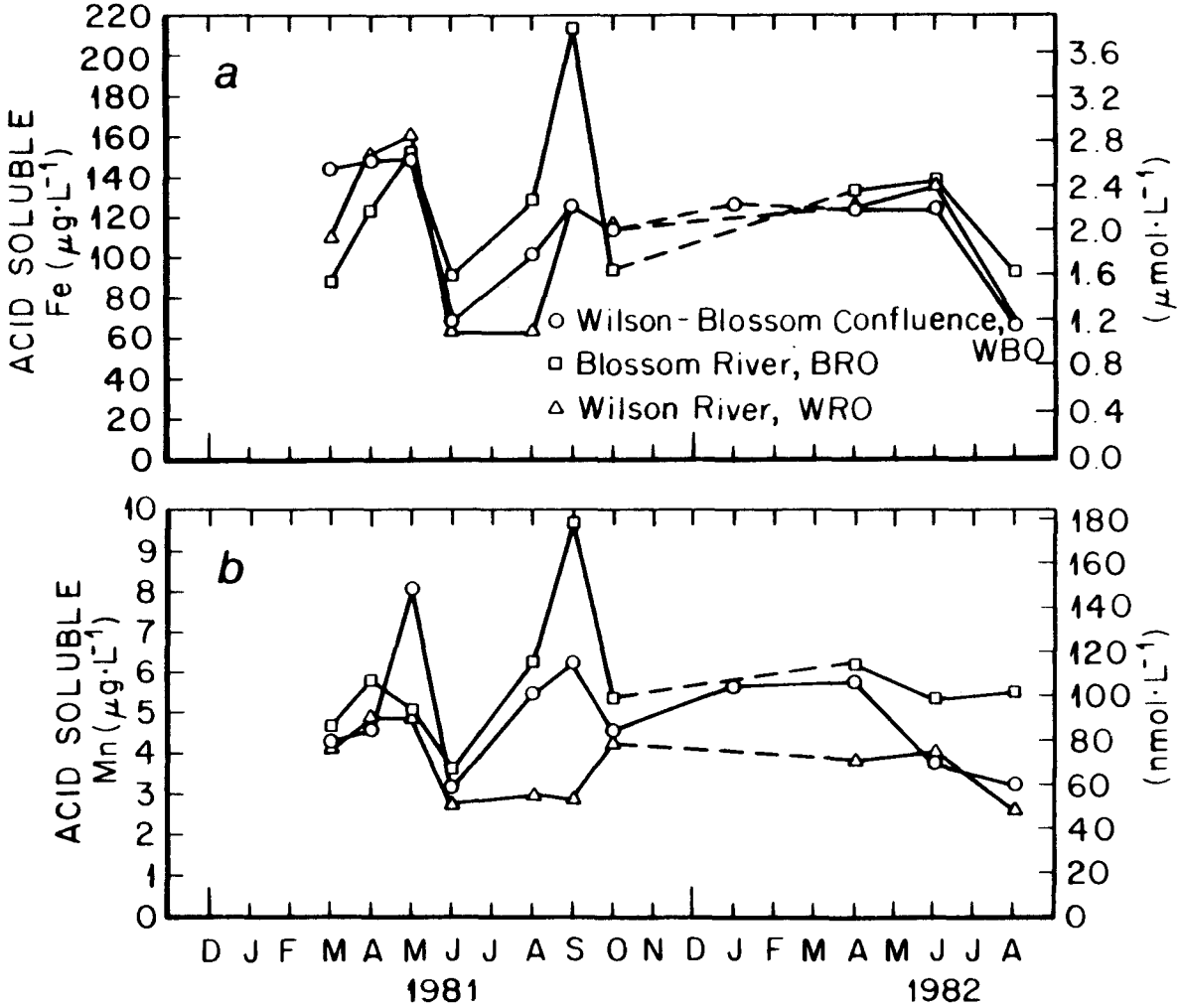


Fig. 6. a. Acid-soluble Fe vs. time for Wilson-Blossom confluence, Blossom River, and Wilson River.
b. Acid-soluble Mn vs. time for Wilson-Blossom confluence, Blossom River, and Wilson River.

DISCUSSION

Dissolved and Particulate Carbon

Although mean DOC concentrations for the Wilson and Blossom rivers are less than the world average of 5.75 $mgC \cdot L^{-1}$ (Meybeck, 1982), high discharge rates from relatively small basins result in high DOC export to Wilson Arm and Smeaton Bay. The DOC exports of the Wilson and Blossom rivers are exceptionally high compared with other North American rivers with comparable watershed areas, only the Nanaimo River, a sixth-order stream on the east coast of Vancouver Island, British Columbia, has transport rates for DOC that are comparable with the rivers I studied. The Nanaimo River, which drains 894 km^2 of mountainous terrain, transports 14.5 g $C \cdot m^{-2} yr^{-1}$ as DOC (Naiman and Sibert, 1978), which is roughly equivalent to the export I obtained for the Wilson River. Because the Nanaimo River has some hydrologic characteristics similar to my study area, I have presented chemical exports from this river with those I obtained from the Wilson and Blossom rivers (Table 5).

Of the two rivers studied, the Wilson River has a lower gradient basin and more watershed area below the tree line (Table 1); this results in the high DOC concentrations and lower pH values found in the Wilson River. In addition, the DOC:POC ratio for the Wilson River is generally greater than for the Blossom River, suggesting that biological processing of particulate organic material within Wilson Lake may be occurring. The DOC:POC ratios observed in this study are

similar to those reported for tundra and wetlands (Schlesinger and Melack, 1981).

Nutrients

The seasonal pattern for transport of ammonia, phosphate, and nitrate + nitrite reflects not only the bimodal discharge pattern but also the significant nonweathering source of ammonia and phosphate. The ammonia concentration pattern we observed in the Wilson and Blossom rivers (Fig. 4b) is unlike that in the Nanaimo River (Naiman and Sibert, 1978), where maximum ammonia concentrations occur in January and April. The late summer ammonia peaks in the Wilson and Blossom rivers are also seasonally anomalous when one considers the ratio NH_4-N/DIN (where DIN is the total dissolved inorganic nitrogen, NH_4-N + NO_2-N + NO_3-N). Meybeck (1982) determined that a median value of NH_4-N/DIN for unpolluted rivers is likely to be approximately 0.15 and for unpolluted precipitation 0.55. The measured rainfall NH_4-N/DIN ratio for the Wilson-Blossom watersheds is 0.44 in March 1981 and 0.30 in September 1981. The river ratio is less than Meybeck's median value except for the late summer-early fall period. In September 1980, August 1981, and August 1982, the NH_4-N/DIN ratio is approximately 0.6 for all river stations. This ratio is approximately 0.04-0.1 for the Nanaimo River in August and September. Because in pristine waters ammonia is present when nitrogenous organic matter is decomposing, possible sources are terrestial plant material and spawning salmon that return to these rivers between late July and September.

In 1980 and 1982, the seasonal phosphate pattern parallels

ammonia for both the Wilson and Blossom rivers (Fig. 4c), with maximum phosphate occurring at a time when DOC (Fig. 4a) and stream flow (Fig. 3) are relatively low. I believe that decomposition of spawned salmon is the most likely explanation for the observed nutrient peaks because (1) the DOC export from the terrestrial environment is low during the brief drought period in late summer, (2) calculations show that salmon can account for the observed concentrations, and (3) streams without salmon do not exhibit ammonia and phosphate peaks in late summer.

The importance of salmon carcass decomposition on the phosphorus cycles of a subalpine stream (Richey et al., 1975) and an Alaskan lake (Donaldson, 1967) has been demonstrated. Richey et al. (1975) calculated that a spawning population of 14 000 sockeye salmon (*O. nerka*) are responsible for an increase of phosphorus of 4.3 $ug \cdot L^{-1}$ in Taylor Creek, California, during the period December-March. They reported that this calculated increase compares well with a measured difference of 6 $ug \cdot L^{-1}$ between upstream (no salmon) and downstream phosphate. I suggest that the much larger numbers of predominately pink salmon in the Wilson and Blossom rivers are largely responsible for the August-September increases in nutrient concentrations.

The Alaska Department of Fish and Game conducts aerial surveys of major salmon streams on a weekly or biweekly basis throughout the major spawning period. Their peak escapement numbers represent the highest 1-d count of salmon based on these surveys. The peak escapement values for the 1980 season were 192 000 mixed pink and chum salmon for the Wilson River on August 3 (4 d before my August river sampling) and 65 800 for the Blossom River on August 12 (5 d after my

sampling). These numbers are somewhat misleading because fish observed in the area seaward of the confluence of the Wilson and Blossom rivers are counted as Wilson River spawners when in fact a significant portion of the fish will spawn in the Blossom River. Thus, the peak escapement numbers may underestimate fish returning to the Blossom River. In the 1981 season, the peak escapement to the Wilson River was 135 000 on August 18 (6 d after my sampling) whereas the Blossom River peak was 51 400 occurring on August 8 (3 d before my sampling). In the 1982 season, the peak escapement for both rivers occurred on August 16 (9d before my river sampling) and was 188 000 for the Wilson and 116 000 for the Blossom (P. Doherty, Alaska Department of Fish and Game, Ketchikan, AK, personal communication). Because of the large number of fish in the river at one time and because pinks die within a few days after spawning, it is often difficult to discern live from dead fish in aerial surveys. However, to illustrate the rapid demise of the spawning salmon, a survey by foot of the Blossom River on August 31, 1981 (23 d after the peak escapement of 51 400), reported 2367 dead salmon out of 6434 total fish (Jones and Dangel, 1982).

To make a rough calculation of the potential nutrient flux due to decomposing salmon, I let 3×10^5 fish represent a combined Wilson-Blossom fish count for August 1982. The mean flow rates for these rivers are 20.4 and 12.9 $m^3 s^{-1}$, respectively. Assuming that most decomposition occurs within a month, then 8.9×10^{10} L of river water will be affected. Mature pink salmon weigh between 1.36 and 3.18 kg and are the smallest of the salmon species. Thus, I assume the

average fish in a mixed pink and chum assemblage is 2.3 kg and composed of 1.3% nitrogen (Parsons et al., 1977) and 0.38% phosphorus (Donaldson, 1967). Therefore, an order of magnitude measure of the potential input of nitrogen and phosphorus from decomposing salmon is 0.1 mg $N \cdot L^{-1}$ (7.2 $umol \cdot L^{-1}$) and 29 ug $P \cdot L^{-1}$ (0.9 $umol \cdot L^{-1}$), respectively. Although it can be argued that a portion of the returning salmon is consumed by predators and scavengers (e.g. bears, eagles, ravens, gulls, seals), my calculations indicate that the potential salmon-supplied nitrogen and phosphorus can account for the observed increases in ammonia and phosphate concentrations.

I believe that the salmon must contribute significantly to the nutrient export from the Wilson and Blossom rivers because in addition to my rough calculations, I have not observed a similar nutrient increase in streams without salmon. The stream draining Lake 793 (station 793-1 on Fig. 1) does not support salmon because of steep falls above Wilson Arm but does receive large quantities of terrestrially derived DOC. On August 27, 1982, this station contained a 6.8 mg $C \cdot L^{-1}$ as DOC but only 0.05 umol phosphate$\cdot L^{-1}$ and 0.25 umol $ammonia \cdot L^{-1}$.

Trace Metals

Of the three trace metals examined, the river concentrations of acid-soluble Cu were low and flow dependent; the concentrations of acid-soluble Fe and Mn were higher and more seasonally variable than Cu. More of the acid-soluble Cu was in the dissolved form for the Wilson River than for the Blossom River, suggesting that Wilson Lake

may retain or solubilize particulate Cu as well as POC. Biological reduction of Mn oxides and Fe oxides during decomposition of organic matter in muskeg ponds is probably responsible for seasonally high river concentrations of Mn and Fe. The highest concentrations of acid-soluble Fe and Mn were obtained from a sample collected at WM-2, a muskeg pond in the Wilson River watershed on October 16, 1981. Conditions in the pond were highly reducing (hydrogen sulfide was present) with much suspended material in the water. On that day, the acid-soluble Fe concentration was 10 560 $ug \cdot L^{-1}$ (189 $umol \cdot L^{-1}$) and the acid-soluble Mn concentration was 71.5 $ug \cdot L^{-1}$ (1.3 $umol \cdot L^{-1}$).

Effects of River-Derived Organic Matter on Transport of Trace Metals to Smeaton Bay

The amount and lability of organic material available to rivers and streams draining into Wilson Arm and Smeaton Bay appear to influence the extent of metal transport to, and reactions within, the freshwater-estuarine mixing zone. In the absence of primary productivity, dissolved phosphate in the freshwater-estuarine mixing zone can be described by conservative (Boyle et al., 1974), two end-member dilution processes (Fig. 7a). Samples collected on October 16, 1981 show a linear increase in phosphate (R^2= 0.90) with increasing salinity. The behavior of Fe is less clear. Acid-soluble Fe decreases only slightly with increasing salinity (Fig. 7b), in contrast with the large-scale removal of metals in (Eaton, 1979) or near the river's mouth that has been observed elsewhere (e.g. Boyle et al., 1977a; Sholkovitz, 1978; Bale and Morris, 1981; Wilke and Dayal, 1982). This suggests that flocculation does not rapidly remove Fe

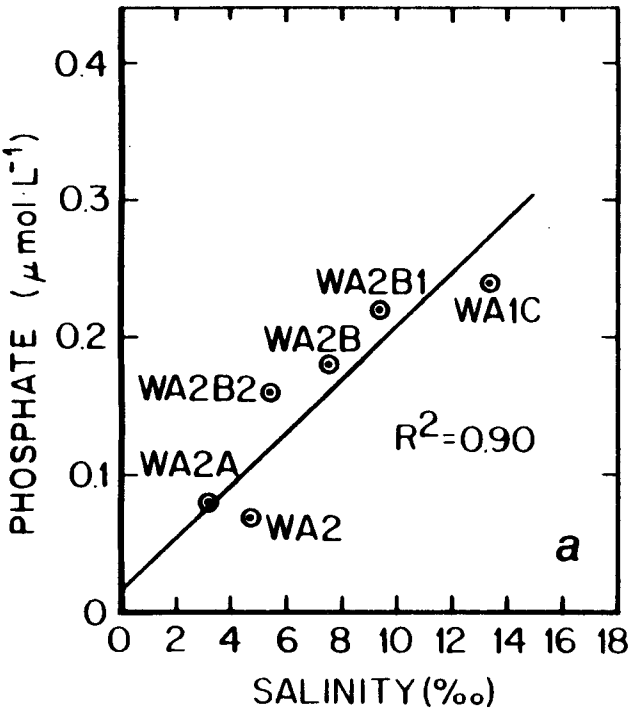
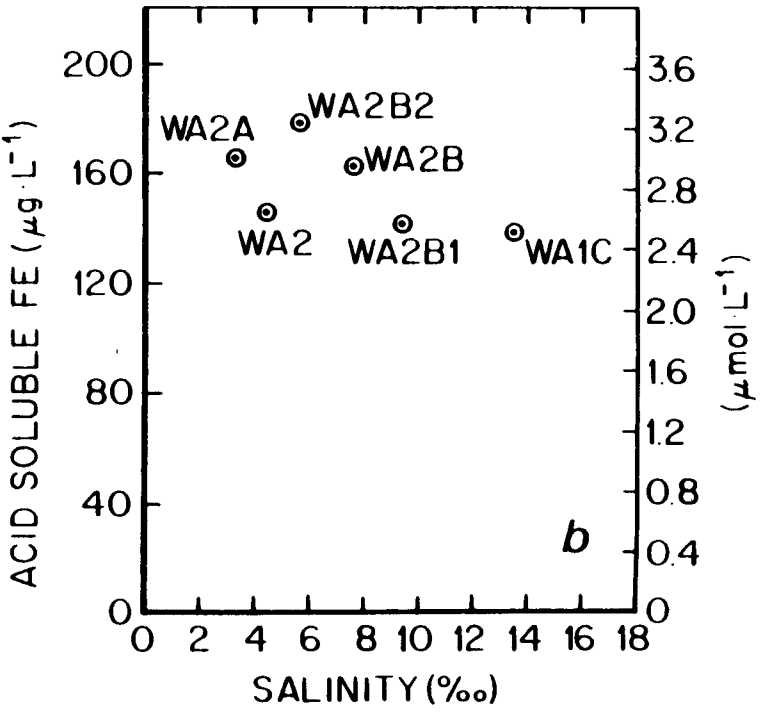


Fig. 7. a. Dissolved inorganic phosphate vs.
b. Acid-soluble Fe vs. salinity.



salinity for stations in Wilson Arm, October 16, 1981.

from fjord waters, a situation observed by Mayer (1982) in the Gulf of Maine. Additional evidence for the importance of organics in retaining Fe in solution was obtained on August 5, 1981, the day of a heavy summer rain after an extended drought period. After the rain stopped, acid-soluble Fe concentration at station WA2B was 272 $\pm$ 0 $ug \cdot L^{-1}$ (Fig. 2). The Fe concentrations at WA2 and WA1 were 251 $\pm$ 1 and 246 $\pm$ 14 $ug \cdot L^{-1}$, respectively. Water from SB1 on the following day had an acid-soluble Fe concentration of 164 $\pm$ 2 $ug \cdot L^{-1}$. Clearly, a mechanism exists for transporting Fe throughout and perhaps beyond the fjord system.

Possible Consequences of Transport

The timing of exports of DOC, nutrients, and trace metals in the Wilson-Blossom system, observed in the 1981-1982 water years, may be optimum for perpetuating an ecosystem suitable for salmon survival. Higher levels of ammonia and phosphate are made available to intertidal areas at the same time that humic concentrations are the lowest. The presence of intensely colored, dissolved humics in the surface waters of Wilson Arm severely reduces primary productivity relative to that in areas farther from freshwater influence. It may restrict primary productivity in the intertidal region to an equal or greater extent. In August 1982, the surface carbon uptake rate was 4.32 $\pm$ 0.24 mg $C \cdot L^{-1}h^{-1}$ at WA2 (Fig. 2) compared with 1.68 $\pm$ 0.47 mg $C \cdot L^{-1}h^{-1}$ at SB1, a station with much higher seasonal carbon uptake. I suggest that this increased late summer productivity may be a response to the river-supplied nutrients. Another consequence of the flow

regime in the Wilson and Blossom rivers is that the concentration of Cu, a potentially toxic metal, is low during low discharge periods. Because the net effect of decreased river flow is an increase in water residence time, it is desirable that metals such as Cu be low, especially since humic compounds capable of making the Cu biologically unavailable are at a minimum during low-flow periods.

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3. Effects of Physical Mixing Upon Geochronologies and Trace Metal Distributions in Sediment from Two Southeast Alaskan Fjords

Abstract- The influence of physical mixing upon the sediment from two pristine fjords in southeast Alaska was examined by determining the ^{210}Pb, ^{137}Cs, and trace metals distributions in cores collected from terrestrially-influenced and basin locations. In the shallower areas of the fjords, non-linear log ^{210}Pb profiles and enhanced ^{137}Cs penetration depths suggest a substantial terrestrial contribution, and sediment mixing coefficients ranging from >6.6 to >65 cm^2yr^{-1}. Sediment focusing and reduced mixing in the basin areas result in linear log ^{210}Pb distributions with apparent accumulation rates of 88 $\pm$15 mg $cm^{-2}yr^{-1}$ and reducing conditions near the sediment-water interface. Comparisons between sediment accumulation rates obtained from 2-layer and constant specific activity models indicate that at some shallow locations erosion and/or deep mixing has occurred. At one basin site in Smeaton Bay, an episodic slump of approximately 10 cm of material is documented by ^{210}Pb, ^{137}Cs, and trace metal profiles taken over a period of 2 years. These data suggest that time-averaging of physical mixing events in fjords can be treated by simplified mixing models formulated for bioturbation, as long as sedimentation rates are relatively high and ancilliary data are available to verify assumed mixing processes.

INTRODUCTION

Interest in the fate of reactive chemical species in recently deposited sediments has resulted in the need for accurate sediment

accumulation rates. ^{210}Pb and ^{137}Cs geochronologies have been used with varying degrees of success to examine recent sedimentary processes in a number of different environments (Livingston and Bowen, 1979; Smith and Walton, 1980; Carpenter et al.,1981; Beasley et al., 1982; Chanton et al.,1983). Because the supply of ^{210}Pb to the marine environment is usually assumed to be steady state over the time scale of decades, while the introduction of bomb-produced ^{137}Cs is highly time dependent, comparing profiles of these two tracers can give independent estimates of sediment accumulation. However, ^{210}Pb and ^{137}Cs distributions in estuarine sediment can be influenced by: (1) episodic deposition of sediment by slumping or major storms, (2) erosional events such as scouring or dredging, (3) homogenization of sediment by physical or biological mixing, and (4) seasonal variations in deposition of terrestrially-derived material. Such non-steady state processes may preclude accurate sedimentation rate determinations, but understanding their effects upon geochronologies gives information on processes affecting sediment in these dynamic systems. In this chapter, I report the influence of physical mixing upon the ^{210}Pb, ^{137}Cs, and trace metal distributions in sediment from two pristine fjord-estuaries in southeast Alaska. High latitude fjords are particularly subject to slumping because of their steep sides and seasonally pulsed inputs of fresh water. However, the depth of the basins, and the low water temperatures throughout the year, minimize the effect of bioturbation. By examining cores from both terrestrially-influenced and deep basin locations, I present data suggesting that time-averaged physical mixing events in fjords with

high sedimentation rates can be treated by existing models formulated for bioturbation.

STUDY AREA

Smeaton Bay and Boca de Quadra (Fig. 1) are two adjacent fjord-estuaries (55°20'N) located in a rugged mountainous region just north of the Alaska-British Columbia border. Smeaton Bay consists of a single 240 m deep basin, defined seaward by a 140 m deep entrance sill, and landward by abrupt shoaling into Wilson and Bakewell Arms. The Wilson and Blossom Rivers meet about 0.8 km from Wilson Arm and provide a mean annual discharge of 53.2 m^3s^{-1} to the 22 km long fjord system. Fresh water input at the head of Bakewell Arm is minimal. Boca de Quadra is a 60 km long, three-basin system which has riverine input from the Keta River at the head, and from the Marten and Red Rivers at the head of Marten Arm. The combined Marten and Red River mean annual discharge of 56 m^3s^{-1} is approximately 2.4 times the mean Keta River flow. Unlike Wilson and Bakewell Arms where the bottom continuously shoals from Smeaton Bay, Marten Arm consists of a 208 m basin that shoals in both landward and seaward directions. The deep (370 m), central basin of Boca de Quadra is separated from the well-mixed outer basin by a 85 m deep sill. Schematic longitudinal profiles of Smeaton Bay and Boca de Quadra with station locations are shown in Fig. 2. Because of the smaller size and less complicated basin structure, Smeaton Bay will be considered in greater detail.

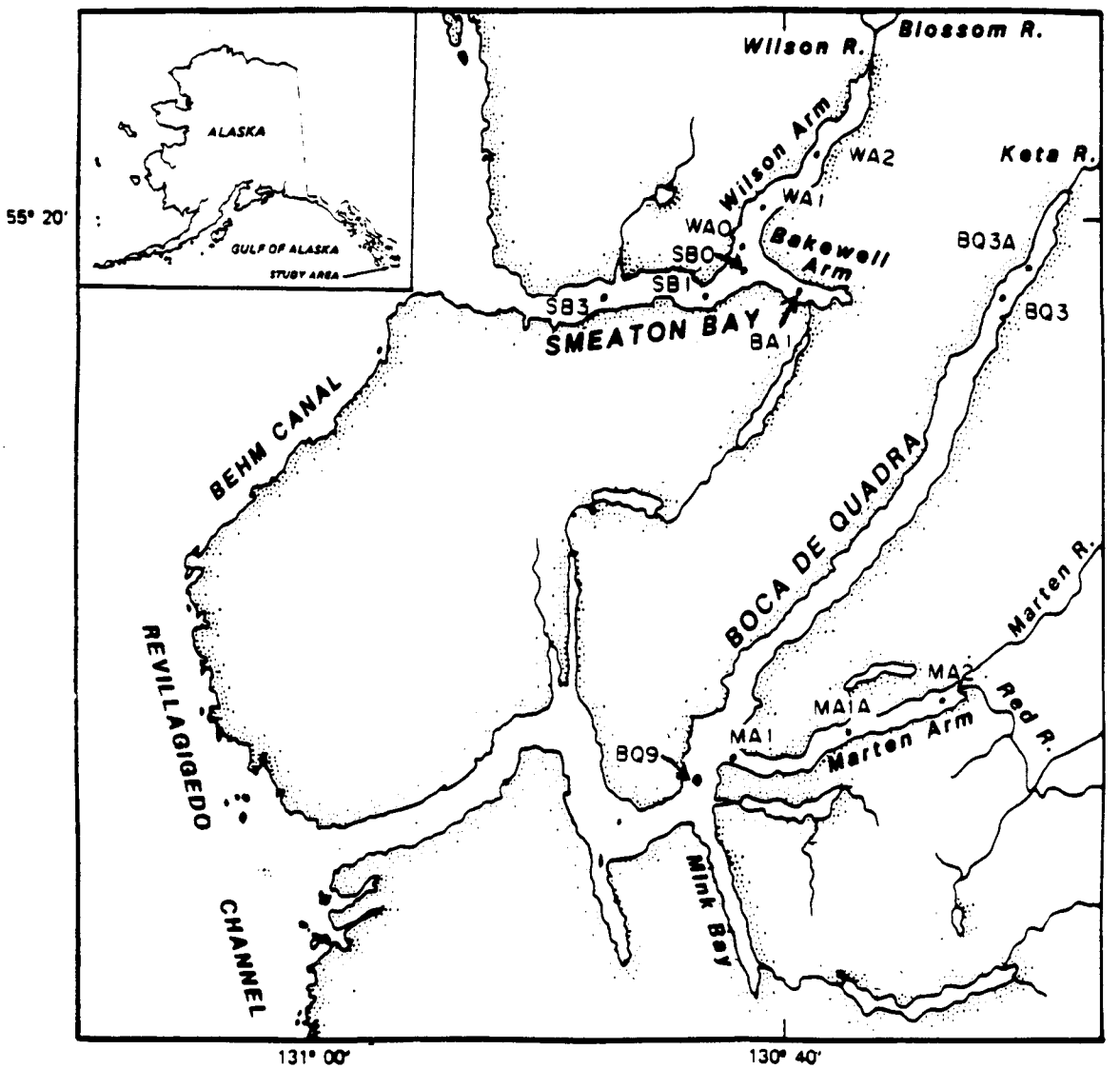

Fig. 1. Location of stations in study site.

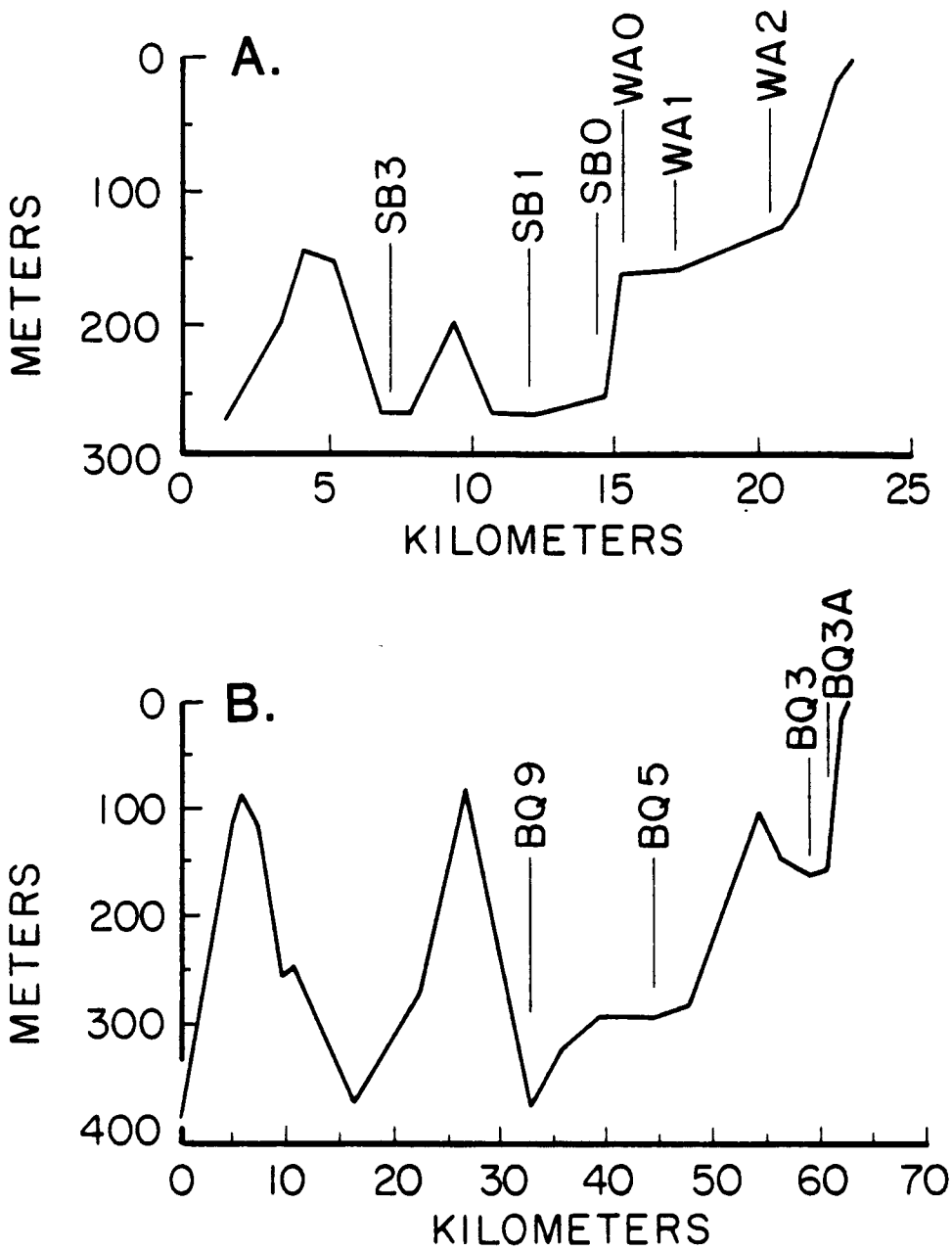

Fig. 2. Longitudinal profiles and station locations for (a) Smeaton Bay and (b) Boca de Quadra.

METHODS AND MATERIALS

Sampling Methods

The sediment samples were collected using a Benthos gravity corer with 6.7 cm i.d. plastic core liners without core catcher, nose cone, or pipe barrel. Cores collected for ^{210}Pb, ^{137}Cs, and porosity were sectioned immediately and frozen for later analysis. Cores collected for interstitial water were extruded directly into PVC (Reeburgh, 1967) squeezers constructed with internal diameter virtually identical to that of the core liner, thereby minimizing atmospheric exposure. Interstitial water was squeezed from the sediment using 5-30 psi of ultrapure nitrogen gas at reduced temperatures. Two pre-combusted Whatman EPM 1000 filters were used in the squeezers. The initial several mL of the interstitial water removed from each section were discarded. Samples for Fe and Mn were collected in acid-washed, linear polyethylene bottles, acidified with ultrex HCl and stored frozen.

Analytical Techniques

To determine ^{210}Pb activity, ^{210}Po, an alpha-emitting daughter was extracted from the sediment and counted. Because laboratory analyses were begun at least 5 months after collection, secular equilibrium between ^{210}Po ($t_{1/2}$=138 d) and ^{210}Pb ($t_{1/2}$=22.2 yr) was assumed. A 2- to 3-g aliquot of dried sediment was spiked with ^{208}Po (chemical yield tracer), leached twice with concentrated HNO_3 and HCl, and centrifuged twice. The leachate was then evaporated to dryness, and the residue converted to chlorides by repeatedly adding HCl and

evaporating to dryness. The residue obtained after leaching the sediment was dissolved in approximately 250 mL of 0.3 M HCl, and ascorbic acid added to complex the Fe in solution. The ^{210}Po was spontaneously electroplated onto 2.2-cm silver discs (one side coated with an insulating varnish) overnight. These discs were rinsed with distilled water, dried, and alpha-counted for ^{208}Po and ^{210}Po using Si surface-barrier detectors and alpha pulse-height analysis spectroscopy. Unsupported ^{210}Pb values were determined by subtracting the mean of two or three ^{210}Pb values taken from 40 to 80 cm deep in the core, where excess ^{210}Pb was depleted. Porosity was calculated from sediment sample weights before and after drying at 60°C, assuming a density of 2.5 g cm^{-3}. All weights were salt corrected.

^{137}Cs activities were obtained from gamma-counting approximately 6 g of dried sediment with a Ge(Li) detector and multi-channel analyzer. Counting errors reported are $\pm$ 1 S.D.

Interstitial Fe was analyzed using the ferrozine technique of Stookey (1970) as applied to natural waters by Murray and Gill (1978) and Gibbs (1979). Interstitial Mn was determined by direct injections of 1:100 dilutions of interstitial water samples into a Perkin-Elmer model 360 atomic absorption spectrophotometer with HGA 2100 furnace.

Calculations

Sediment activities are reported as functions of cumulative mass per unit area (g cm^{-2}) to eliminate the effect of porosity changes with depth. ^{210}Pb mass sedimentation rates were calculated using a one-dimensional, two-layer sedimentation model. All mixing was treated as a time-averaged diffusive process assumed to be confined to

a uniformly mixed surface-layer. The sediment accumulation rate, r, in g $cm^{-2}yr^{-1}$, was determined from the expression, $r = -b/\lambda$, where b is the slope of the least squares fit to the natural log (unsupported ^{210}Pb) versus cumulative mass curve below the surface mixed layer (SML), and λ is the decay constant of ^{210}Pb in yr^{-1}. The thickness of the SML was estimated by visual inspection of the ^{210}Pb profiles or by the intersection of the SML with the best least squares fit for the remaining points.

Mixing coefficients within the SML, K_b, were calculated assuming that compaction effects are negligible, and that the distribution of ^{210}Pb can be described by an advection-diffusion equation (Robbins, 1978) of the form:

$$\frac{\partial A}{\partial t} = \frac{\partial}{\partial z}\left(K_b \frac{\partial A}{\partial z}\right) - w\left(\frac{\partial A}{\partial z}\right) - \lambda A = 0 \qquad (1)$$

where A= excess ^{210}Pb activity, dpm g^{-1}

K_b= mean mixing coefficient, cm^2yr^{-1}

λ = decay constant of ^{210}Pb, yr^{-1}

w= sediment accumulation rate, cm yr^{-1}.

The first term on the right-hand side of eq. (1) represents the rate of change of activity at depth, z, due to effects of mixing, the second term accounts for sediment accumulation, and the third term for radioactive decay.

Solving eq. (1) for w, the accumulation rate gives:

$$w = \frac{\lambda z}{\ln\left(\frac{A_o}{A_z}\right)} - \frac{K_b}{z} \ln\left(\frac{A_o}{A_z}\right) \qquad (2)$$

where A_o= activity of ^{210}Pb at the surface

A_z= activity of ^{210}Pb at depth z positive below the interface.

If mixing is intense and accumulation is slow (i.e. $w^2 << \lambda K_b$), eq. (2) can be used to evaluate the mixing coefficient:

$$K_b = \lambda \left(\frac{z}{\ln \left(\frac{A_o}{A_z} \right)} \right)^2 \qquad (3)$$

Sediment inventories of excess ^{210}Pb and ^{137}Cs were determined by summing the product of the measured activity in dpm g^{-1} and the cumulative mass for each section. Calculated surface ^{210}Pb activities were obtained from extrapolation of the natural log (unsupported ^{210}Pb) versus cumulative mass curve to zero mass. The predicted depth of ^{137}Cs penetration was determined from the sum of the SML thickness plus the product of the ^{210}Pb sedimentation rate multipled by 30 yr (assuming the introduction of ^{137}Cs to these fjords was in 1952).

RESULTS

The sediment characteristics of Smeaton Bay and Boca de Quadra fjords are shown in Table 1. All cores were collected between August 23 and September 7, 1982, except for the core at BQ5 which was collected on April 12, 1983. The stations are grouped into two categories: 1) basin stations: SB0, SB1, SB3, BQ5, MA1A, BQ9, 2) relatively shallow, terrestrially-influenced stations with deep SML's: WA2, WA1, WA0, BA1, BQ3A, BQ3, MA2, MA1. The ^{210}Pb and ^{137}Cs activities and porosities at various depths in each core are tabulated in Appendix A.

Table 1. Sediment characteristics in Smeaton Bay and Boca de Quadra

Location Station	Water depth m	^{210}Pb Surface activity Obs'd dpm g^{-1}	^{210}Pb Surface activity Calc'd dpm g^{-1}	^{210}Pb Two Layer Model SML cm	^{210}Pb Two Layer Model Sedimentation rate cm yr^{-1}	^{210}Pb Two Layer Model Sedimentation rate g $cm^{-2}yr^{-1}$	^{210}Pb Two Layer Model Mixing coef cm^2yr^{-1}	^{210}Pb CSA Model Sedimentation rate g $cm^{-2}yr^{-1}$	^{210}Pb Inventory dpm cm^{-2}	^{137}Cs Penetration depth Obs'd cm	^{137}Cs Penetration depth Calc'd cm	^{137}Cs Inventory dpm cm^{-2}
Basin Stations												
SB0	241	18.04	15.8	0.0	0.41	0.112		0.079	52.6	15.4	12.3	4.62
SB1	252	14.37	16.5	1.7	0.34	0.082		0.063	42.2	13.8	11.9	3.19
SB3	259	14.39	19.4	2.8	0.31	0.089		0.077	51.4	11.9	12.1	4.25
BQ5	275	13.12	19.3	3.2	0.29	0.063		0.053	35.0			
MA1A	208	14.34	16.1	4.8	0.27	0.091		0.070	46.4	14.0	12.9	8.38
BQ9	368	20.84	20.4	0.0	0.46	0.090		0.082	54.7	11.5	13.8	3.85
Terrestrially-Influenced Stations												
WA2	127	8.63	197.5	17.1	0.12	0.064	12.7	0.063	42.0	21.8	20.7	10.95
WA1	152	11.37	54.2	12.7	0.12	0.054	6.6	0.050	33.6	16.5	16.3	5.92
WA0	162	6.95	9.02	4.7	0.22	0.101	65.0	0.045	30.2	10.8	11.3	3.71
BA1	156	10.12	32.3	10.4	0.12	0.053	23.2	0.047	31.4	14.1	14.0	3.77
BQ3A	145	5.55	2750	17.3	0.07	0.041	11.6	0.048	32.0			
BQ3	156	6.82	13.1	10.4	0.26	0.137	26.3	0.061	40.4			
MA2	175	7.68		>27.3			>15.8					
MA1	174	7.02	289	7.0	0.04	0.023	14.8	0.041	27.2	12.5	8.2	4.52

The ^{210}Pb sediment accumulation profiles for basin areas of Smeaton Bay and Boca de Quadra are remarkably similar and are shown in Fig. 3a. The mean surface ^{210}Pb activity is 15.8 $\pm$ 3.0 dpm g^{-1} (n=6) with an average sedimentation rate of 88 $\pm$ 16 mg $cm^{-2}yr^{-1}$. Equivalent profiles for the shallower stations are shown in Figs. 3b and 3c where a deep (>13.3 $\pm$ 7.1 cm, n=8) surface mixed layer is observed, and the average surface ^{210}Pb activity is 8.0 $\pm$ 1.9 dpm g^{-1} (n=8); the sedimentation rate below the SML for these shallower areas is 68 $\pm$ 39 mg $cm^{-2}yr^{-1}$ (n=7). K_b, the mixing coefficient, ranged from $\geq$ 65.0 cm^2yr^{-1} at WA0 to $\geq$6.6 cm^2yr^{-1} at WA1. Near the Marten River outfall, the mixed layer extends to greater than 27 cm depth at MA2 (Fig. 3c), and has a very irregular profile which precludes determining a ^{210}Pb sedimentation rate. At the other shallow station in Marten Arm, MA1, we found the lowest ^{210}Pb sedimentation rate (23 mg $cm^{-2}yr^{-1}$) and inventory (27.2 dpm cm^{-2}) of the studied area. The highest observed inventory was 54.7 dpm cm^{-2} at BQ9 in the deep basin of Boca de Quadra.

Profiles of ^{137}Cs activities versus cumulative mass for the basin and shallower areas are shown in Figs. 3d and 3e. ^{137}Cs is observed to depths of 21.8 cm at WA2, the station closest to the Wilson-Blossom River; at BQ9 and SB3, in the basins of Boca de Quadra and Smeaton Bay, ^{137}Cs is restricted to the upper 11.5 and 11.9 cm, respectively. The highest ^{137}Cs inventories are found at WA2 and MA1A, sites near river input, and the lowest within the deep basin of Smeaton Bay at SB1.

Solid phase Mn and Cu in sediment from one shallow site in Wilson

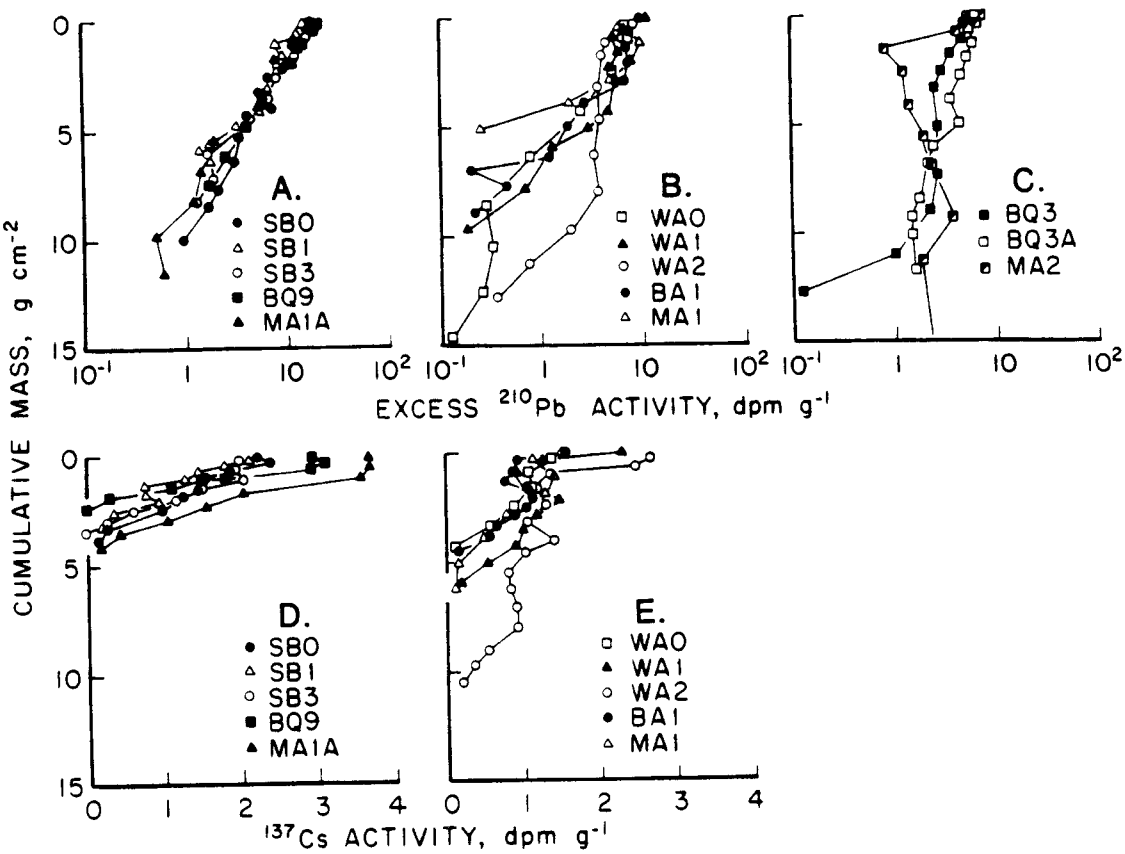

Fig. 3. a. Excess ^{210}Pb vs. cumulative mass for basin stations, August 1982.
b. Excess ^{210}Pb vs. cumulative mass for shallower stations.
c. Excess ^{210}Pb vs. cumulative mass for shallower stations from Boca de Quadra.
d. ^{137}Cs vs. cumulative mass for basin stations.
e. ^{137}Cs vs. cumulative mass for shallower stations.

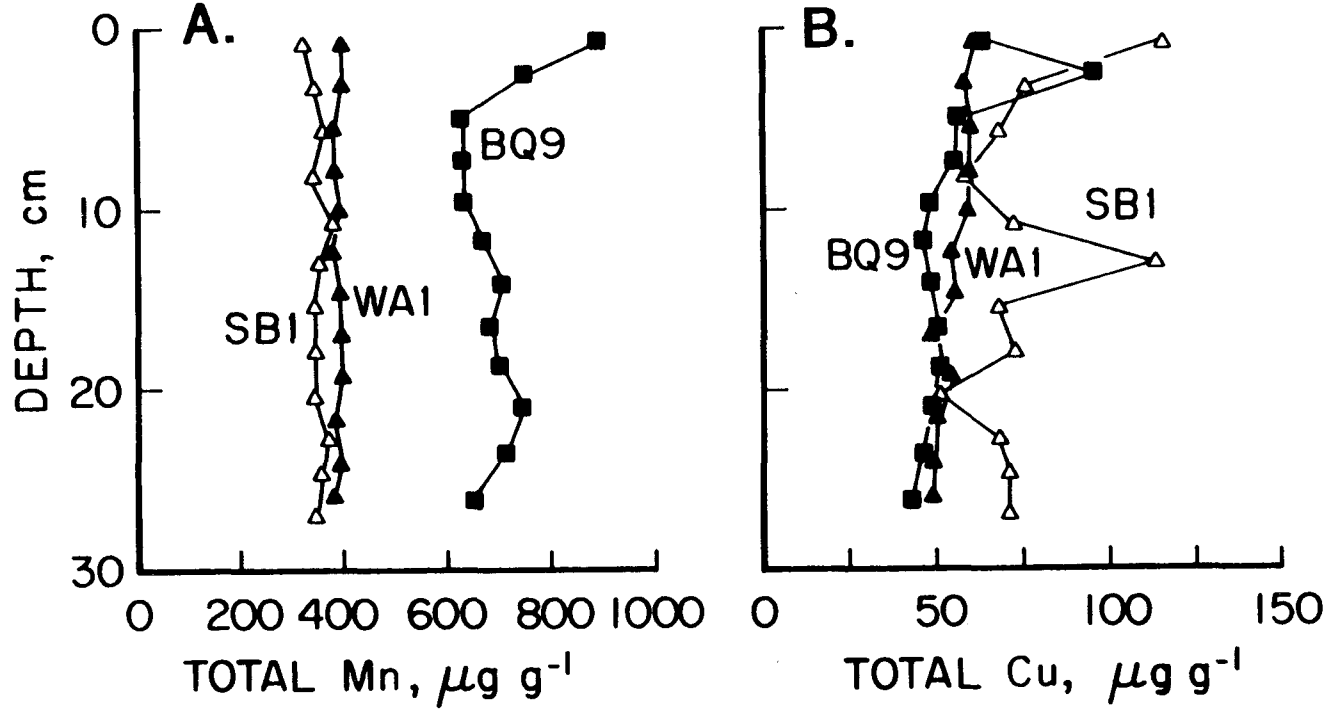

Fig. 4. a. Total sediment Mn vs. depth for stations WA1, SB1, and BQ9, August 1982.
b. Total sediment Cu vs. depth.

Arm, WA1, and two basin stations, SB1 and BQ9, are shown in Fig. 4. While sediment from BQ9 shows an intense peak in solid phase Mn concentrations in the surficial sediments, Mn concentrations in WA1 and SB1 are much lower and more constant with depth. Solid phase Cu has a subsurface maximum of 96 $\pm$ 3 ug g^{-1} at BQ9 that is not observed at WA1. However, at SB1, Cu levels are 116 $\pm$ 18 ug g^{-1} at the surface and 114 ug g^{-1} at 13.2 cm.

Interstitial water profiles of Mn and Fe for the same station groupings as Fig. 3 are shown in Fig. 5 and listed in Appendix B. These cores are companion ones to those collected for ^{210}Pb and ^{137}Cs geochronologies in August and September, 1982. At BQ9, in the deep basin in Boca de Quadra, the interstitial Mn concentration is 268 umol L^{-1} in the surficial sediment; at SB0 and SB1, in the main basin of Smeaton Bay, the Mn concentrations in the surface section are approximately 0.1 times that at BQ9 (28.6 and 23.9 umol L^{-1}, respectively). Interstitial water Mn concentrations are much lower at the shallower sites. Highest interstitial Fe concentrations are found in the surficial sediment of SB0 (98.1 umol L^{-1}), and at 3.25 cm in a core collected at WA2 (65.7 umol L^{-1}).

DISCUSSION

Riverine Influences Upon Vertical Distributions and Sediment Inventories of ^{210}Pb and ^{137}Cs

The vertical distributions and inventories of ^{210}Pb and ^{137}Cs in Smeaton Bay and Boca de Quadra sediments vary greatly depending upon location (proximity to river input and side arms) and bottom

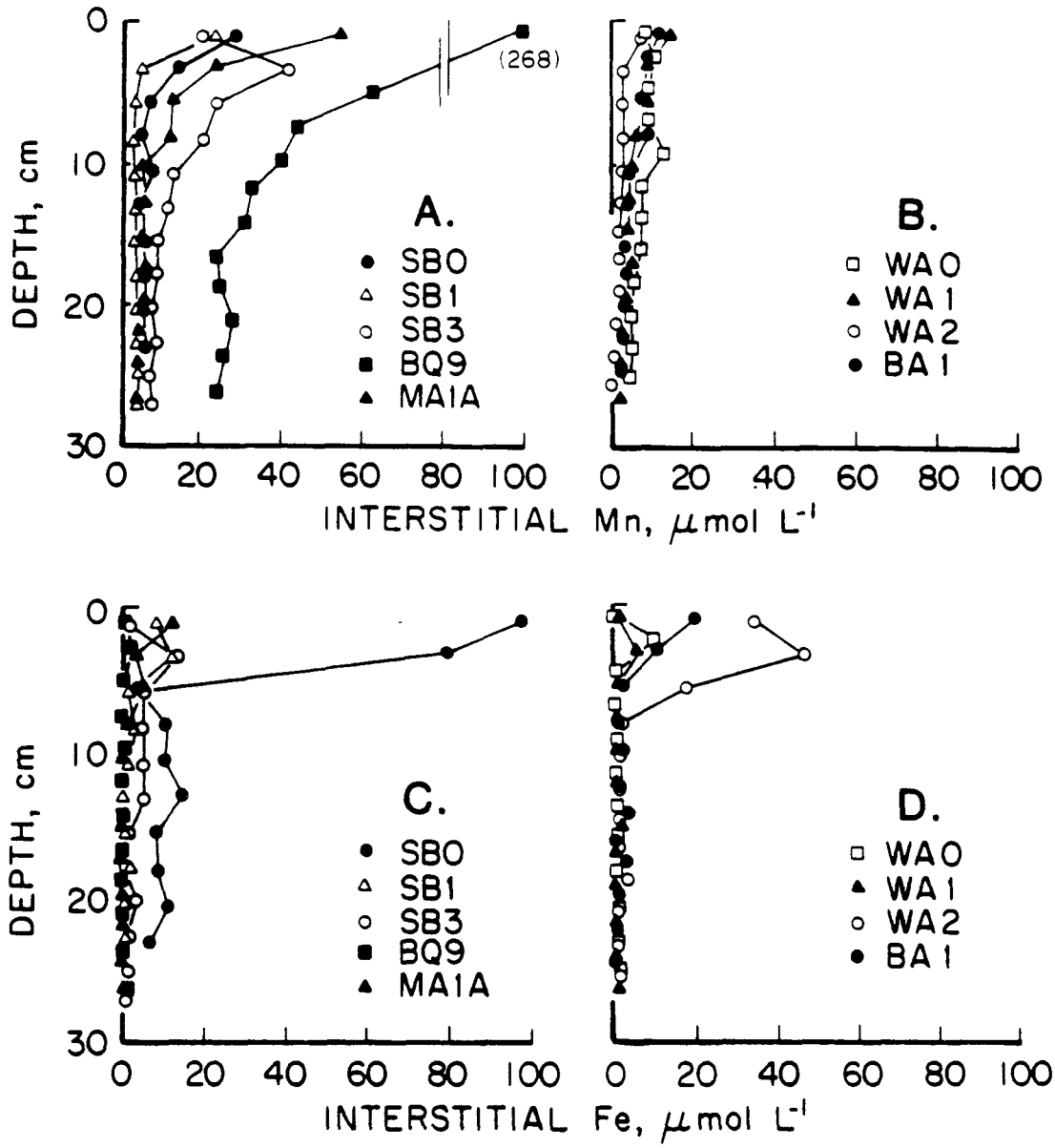

Fig. 5. a. Interstitial Mn vs. depth for basin stations, August 1982.
b. Interstitial Mn vs. depth for shallower stations.
c. Interstitial Fe vs. depth for basin stations.
d. Interstitial Fe vs. depth for shallower stations.

topography (slope of main basin and cross-channel steepness). These two factors determine the sources of sediment, and the intensity and frequency of slumping and/or post-depositional mixing.

In the marine environment, fallout ^{137}Cs is predominately in the dissolved form (Simpson et al., 1976); in freshwater, the major portion is associated with particulate phases. Thus, the source of ^{137}Cs observed in the sediment from Smeaton Bay and Boca de Quadra is primarily fallout ^{137}Cs that has been adsorbed onto clay (predominately, illite and chlorite, M. Robb, Institute of Marine Science, University of Alaska, Fairbanks, AK, pers. comm.) particles in the watershed, and transported to the fjords by rivers and streams. Fig. 6 shows the importance of terrestrial input and physical mixing upon the ^{137}Cs and ^{210}Pb profiles of a relatively shallow, river-influenced station, WA2 (Fig. 6b) compared with a basin station, BQ9 (Fig. 6a). River input of terrestrially-derived sediment results in enhanced ^{137}Cs inventories at stations WA2 and WA1 in Wilson Arm and station MA1A in Marten Arm (Table 1). The highest ^{137}Cs activities occur in recent sediment rather than in sediment deposited in 1963 (peak year in global ^{137}Cs fallout), suggesting a delay in transport of ^{137}Cs from the watershed to these stations. The systematic decrease in ^{137}Cs inventory as one proceeds seaward in Wilson Arm from the Wilson/Blossom River (WA2, WA1, WA0, Fig. 3E) reflects the decrease in terrestrial influence.

Because ^{210}Pb inventories in the basins of Smeaton Bay and Boca de Quadra are greater than expected from atmospheric deposition (32 dpm cm^{-2}: Benninger, 1978), and do not increase steadily with increasing

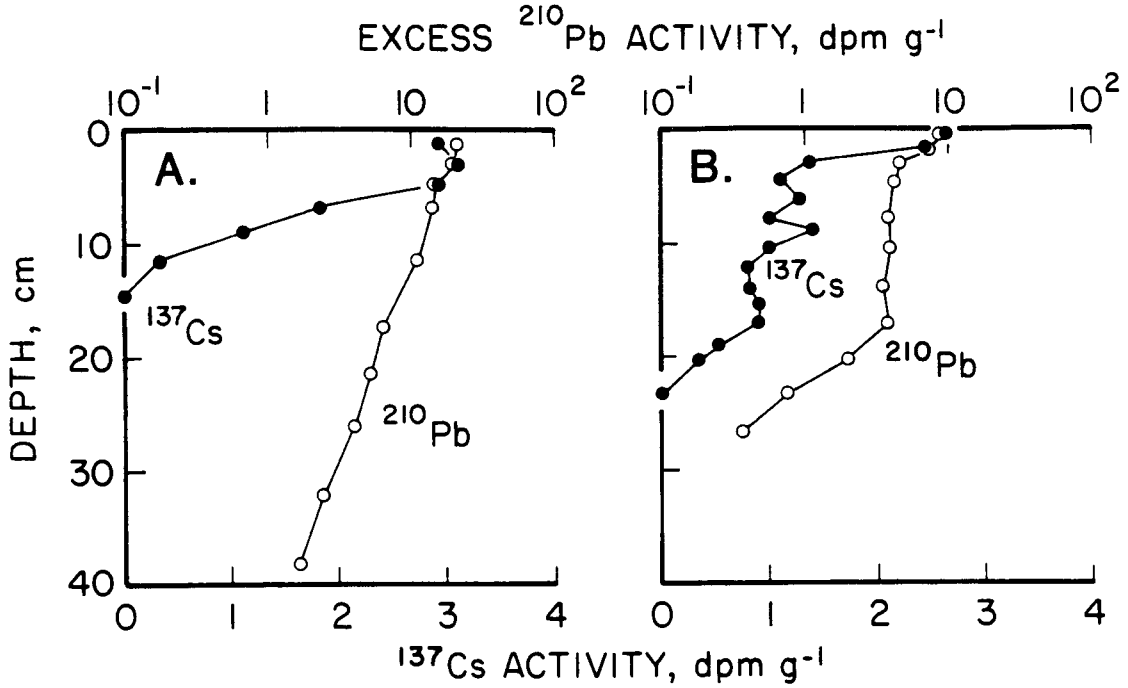

Fig. 6. a. Excess ^{210}Pb and ^{137}Cs vs. depth for basin station, BQ9, August 1982.
b. Excess ^{210}Pb and ^{137}Cs vs. depth for river-influenced station, WA2.

water depth (expected if steady state production from ^{226}Ra in the overlying water were the dominant process), horizontal transport of sediment is indicated. The highest inventories occur at BQ9, SB0, and SB3. The sediment inventory at BQ9 is augmented by material from up-fjord, from Marten Arm, and possibly, Mink Bay (Fig. 1). The ^{210}Pb inventory and sedimentation rate at MA1 are low, suggesting that Marten Arm may be a region of net sediment export. Likewise, in Smeaton Bay, SB0 may be a region of sediment focusing of material from Wilson and Bakewell Arms. The surface porosities at MA1 and WA0 (Appendix A) are relatively low (0.851 and 0.873, respectively) which supports the hypothesis that the organic-rich, high porosity surface layers of sediments from Marten and Wilson Arms are transported into the fjord basins (e.g. BQ9 and SB0, which have surface porosities of 0.942 and 0.933).

Comparing the sediment inventories of ^{137}Cs and ^{210}Pb with those expected from atmospheric fallout suggests transport mechanisms, and the ratio of ^{137}Cs to ^{210}Pb inventories indicates relative contributions of terrestrial and marine sediment. Assuming a constant flux of ^{210}Pb to the sediment, the maximum ^{210}Pb activity would be at the surface, and, assuming no post-depositional removal of sediment, the ^{210}Pb inventory will include approximately 100 yr (4-5 half-lives) of sedimentation. ^{137}Cs was first introduced into the atmosphere in 1952 (peak fallout occurred in 1963 and rapidly decreased in subsequent years), and thus the ^{137}Cs inventory has accumulated for only 30 yr. The maximum activity of this bomb-created isotope (corrected for radioactive decay, $t_{1/2}$=30.2 yr), should occur at the

depth corresponding to the peak fallout years. Our data show that ^{210}Pb inventories at the basin stations (BQ9, SB1, SB0, SB3, and MA1A) are in all cases greater than inventories at shallower locations in the fjords, and 1.3 to 1.7 times greater than atmospheric deposition of the isotope. The ^{137}Cs inventories for the basin stations range from 3.19-8.38 dpm cm^{-2}. Using ^{90}Sr data for atmospheric fallout in 10° bands of latitude for the period 1958-1966 (Joseph et al., 1971), I adjust the value of 25.8 dpm cm^{-2} obtained for the integrated 1954-1975 fallout delivery of ^{137}Cs in New York City (41°N) (Olsen et al., 1981a) to obtain an expected 18.0 dpm cm^{-2} for the 50-60°N zone. This indicates that the observed ^{137}Cs inventories in the basin regions of Smeaton Bay and Boca de Quadra (stations SB0, SB1, SB3, and BQ9) are roughly 18-26% of the expected atmospheric fallout values (Table 2). The ^{137}Cs inventory is 61% of atmospheric fallout at station WA2 (approximately 3 km from the Wilson-Blossom River outfall) and 46% of fallout at station MA1A (about 4 km from the Marten-Red River outfall). Comparing the inventory of ^{137}Cs (predominately, terrestial in origin) to that of ^{210}Pb (marine origin), indicates that terrestrial material is about twice as important to the total sediment accumulation of sediment in Wilson Arm (stations WA2, WA1) and Marten Arm (MA1A, MA1) than in Smeaton Bay or Boca de Quadra (Table 2). By contrast, the ratios of ^{137}Cs to ^{210}Pb inventories at shallow stations BA1 in Bakewell Arm (Fig. 1) and WA0 at the seaward extreme of Wilson Arm (Fig. 2a), are approximately equal to the ratios in the main basins of Boca de Quadra (BQ9) and Smeaton Bay (SB1, SB0, SB3). The relatively low terrestrial influence at these stations is probably

Table 2. Comparison of ^{210}Pb and ^{137}Cs inventories in sediments from Smeaton Bay and Boca de Quadra.

Station	$I_{Pb\text{-}210}$ dpm cm^{-2}	$\frac{I_{Pb\text{-}210}}{atm_{Pb\text{-}210}}$	$I_{Cs\text{-}137}$ dpm cm^{-2}	$\frac{I_{Cs\text{-}137}}{atm_{Cs\text{-}137}}$	$\frac{I_{Cs\text{-}137}}{I_{Pb\text{-}210}}$
WA2	42.0	1.31	10.95	0.61	0.26
WA1	33.6	1.05	5.92	0.33	0.18
WA0	30.2	0.94	3.71	0.21	0.12
BA1	31.4	0.98	3.77	0.21	0.12
SB0	52.6	1.64	4.62	0.26	0.09
SB1	42.2	1.32	3.19	0.18	0.08
SB3	51.4	1.61	4.25	0.24	0.08
MA1A	46.4	1.45	8.38	0.46	0.18
MA1	27.2	0.85	4.52	0.25	0.17
BQ9	54.7	1.71	3.85	0.21	0.07
atmospheric	32.0	-	18.0	-	0.56

because of the lack of major fresh water input in Bakewell Arm, and sediment erosion from Wilson Arm to Smeaton Bay.

Riverine Influences Upon Vertical Distributions of Trace Metals

Differences in the interstitial Mn profiles shown for the basin areas (Fig. 5a) versus those for the shallower stations (Fig. 5b) result from the redox conditions imposed by the type of organic matter present, as well as from the frequency of post-depositional mixing. The importance of riverine contributions of dissolved and particulate C is reflected in the C/N ratios of the surficial sediments. Lower C/N ratios are generally observed further from river inputs (stations SB3, SB0, SB1, BQ9) where detritus from N-rich plankton is a significant component of the sedimentary organic matter. The watershed influence on the total carbon inventory of the sediment is two-fold. First, in both fjords, allochthonous organic material is highly refractory and dilutes the reactive carbon. Terrestrial material (wood, spruce needles) is present deep in cores from Wilson, Bakewell, and Marten Arms, and although sediment carbon levels are high, the surface sediments are not anoxic. Secondly, because the fresh waters draining the watersheds in my study area are highly colored and nutrient poor (Sugai and Burrell, 1984), the annual integrated primary productivity is 15 to 35% less in the inner fjord areas (WA1/2, BQ3/3A, MA2) than in the basin areas (SB0/1, BQ9). Because the annual primary productivity in the basin areas of Smeaton Bay and Boca de Quadra (SB1, BQ9) is similar, the observed difference in the sediment redox conditions between the deep areas of the two fjords (demonstrated most dramatically by the solid phase and interstitial Mn

profiles, Figs. 4a and 5a) is believed to result from differences in the frequency of mixing, rather than in the supply of autochthonous organic matter.

Mixing as the result of sediment slumping at BQ9 must be relatively infrequent on the ^{210}Pb time scale, permitting diagenetic remobilization of reduced Mn close to the interface. High concentrations of solid phase Cu and Mn occur near the surface at BQ9 (Fig. 4), and the interstitial concentration of Mn in the surficial sediment reaches 268 umol L^{-1}. By contrast, the solid phase Cu and Mn profiles at WA1 suggest that frequent mixing combined with less labile organic matter prevents reducing conditions from developing. Both the interstitial and solid phase Mn profiles indicate the absence of long term reducing conditions at SB1, but the Cu profile suggests that perhaps the top 10 cm of the core may have resulted from a recent slump of material originally deposited elsewhere. One possible explanation for this observation is that kinetics involved in solubilizing Cu sulfides are much slower than those involved in the oxidation of reduced Fe or Mn.

The interstitial Fe profiles are more difficult to interpret because soluble Fe can form during biological reduction of Fe-oxides or during the abiotic oxidation of metastable Fe-sulfide solids (Aller, 1980). Of the stations sampled, only at BQ9 in the central basin of Boca de Quadra are interstitial Fe concentrations low throughout the core, suggesting that only at this location have conditions remained stable long enough to develop reducing sediment

conditions near the sediment interface, although high concentrations of organic material occur throughout the fjord.

Application of Mixing Models to ^{210}Pb Profiles from Smeaton Bay and Boca de Quadra

In most coastal sediments, vertical mixing by biological or physical processes occurs in the surface zone, resulting in a non-linear log distribution of excess ^{210}Pb. Although biological mixing has been successfully treated by a diffusive analog (e.g. Guinasso and Schink, 1975; Robbins et al., 1979; Olsen et al., 1981b), physical mixing has not (Nittrouer et al., 1984). However, my ^{210}Pb and ^{137}Cs profiles indicate that physical mixing in these fjords may be represented as a diffusive process on the time scale of decades. In the two-layer model used to calculate mass accumulation rates and mixing coefficients, I have parameterized all mixing into a single term, K_b, that is constant within the SML and zero below the mixed zone boundary. Calculations of K_b based upon the change in ^{210}Pb activity in the SML demonstrate that the apparent sedimentation rate at WA2 (located approximately 3 km from the Wilson/Blossom River) is dominated by mixing ($w^2 << \lambda K_b$). The depth of ^{137}Cs penetration observed agrees well with that predicted from the ^{210}Pb sedimentation rate and observed depth of the SML (Table 1).

Mixing of insufficient intensity to create a SML can generate a linear log unsupported ^{210}Pb distribution with decreased slope (Benninger et al., 1979; Benninger and Krishnaswami, 1981). Carpenter et al. (1982) determined that a 2-3 fold overestimation of the true sediment accumulation rates could result from neglecting deep mixing

that was less than 5% of the mixing responsible for the SML. This effect becomes more pronounced at low sedimentation rates when mixing extends to depths where ^{210}Pb activities approach supported levels. To check the validity of my simplified mixing model for pulsed, physical mixing, I used a constant specific activity (CSA) model (Robbins, 1978) where A_s, the undisturbed surface activity of ^{210}Pb was assumed to equal 20.8 dpm g^{-1} as observed at BQ9, the deep basin station in Boca de Quadra where trace metal profiles suggest relatively long term stability. The sedimentation rate, r (g $cm^{-2}yr^{-1}$) can then be estimated from the vertically integrated ^{210}Pb activity, I_{Pb-210} using the expression:

$$r = \frac{\lambda I_{Pb-210}}{A_s} \qquad (6)$$

Sedimentation rates determined assuming constant specific activity are shown in Table 1. For most basin and shallow stations, the sedimentation rates calculated by this method are relatively close to those calculated using the two-layer model. The most notable exceptions are shallower stations WA0 and BQ3, where the sedimentation rate calculated assuming no mixing below the SML is approximately twice that using the constant specific activity model, and shallow station MA1, where the CSA model gives a greater sediment accumulation rate than the two-layer model. This shows that unaccounted mixing will increase the apparent sediment accumulation rates except in cases such as station MA1, where net sediment export has occurred, in agreement with the observed low ^{210}Pb inventory. Hence in a dynamic system

such as the present study area, the ^{210}Pb-derived sedimentation rates are usually upper limits.

Evidence of a Sediment Slump in Smeaton Bay

Although a deep SML is not apparent for the 1982 data in the basin of Smeaton Bay (stations SB0, SB1, SB3), sedimentation rates calculated using the two-layer model are somewhat greater than those using the CSA model, suggesting mixing below the observed SML. At station SB1, I can document the effects sediment slumping and mixing have had on the resultant ^{210}Pb profile.

As seen in Table 1, assuming a SML of 1.7 cm, the sedimentation rate at SB1 is 82 mg $cm^{-2}yr^{-1}$ (R^2=0.952, n=16); assuming a SML of 10.5 cm, the mass accumulation rate is 68 mg $cm^{-2}yr^{-1}$ (R^2=0.956, n=9). I believe that the time-averaged sedimentation rate is closer to the latter value because of earlier ^{210}Pb cores taken at the same station (Fig. 7a). Both cores collected in December 1980 and October 1981 show evidence of deep surface mixing. The ^{210}Pb and ^{137}Cs (Fig. 7b) profiles from October 1981 have higher activities than the 1982 profile. The ^{137}Cs inventory is 4.13 dpm cm^{-2} for the top 11 cm of the October 1981 core, approximately 30% greater than the total inventory in August 1982. The enhanced ^{137}Cs inventory suggests that the top 11 cm of material collected at SB1 in October 1981 was probably material transported from a more terrestrially-influenced site. This agrees well with the solid phase Cu profile (Fig. 4b), which, perhaps fortuitously, shows a second Cu peak at approximately 11 cm. Interstitial water profiles for Fe and Mn (Chapter 4) which

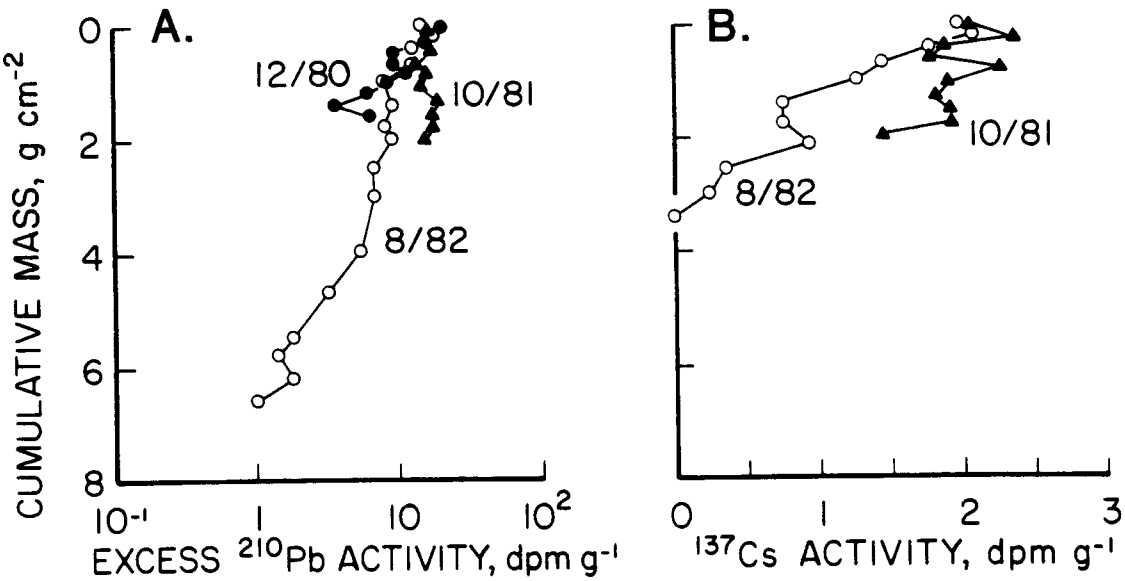

Fig. 7. a. Excess ^{210}Pb vs. cumulative mass for basin station, SB1, December 1980, October 1981, and August 1982.
b. ^{137}Cs vs. cumulative mass, October 1981 and August 1982.

respond more quickly to changes in redox conditions than the solid phase, verify the disturbance suggested by the ^{210}Pb and ^{137}Cs geochronologies.

Comparison of ^{137}Cs and ^{210}Pb Geochronologies

In spite of post-depositional mixing, episodic slumping, and large variability in terrestial and marine sediment inputs, the observed depth of ^{137}Cs penetration is close to that predicted from ^{210}Pb-derived sedimentation rates for most cores (Table 1). The only exceptions are station SB1, in the main basin of Smeaton Bay, where the observed ^{137}Cs penetration depth is less than predicted, and station MA1, in Marten Arm, where the observed penetration depth is greater than predicted. This strongly suggests that fallout ^{137}Cs was rapidly transported to the fjord, since any significant lag-time between introduction of the isotope into the atmosphere and appearance in the sediment would result in an underestimation of the ^{137}Cs sedimentation rate. In addition, my results suggest that ^{137}Cs is not mobile in the sediments of Smeaton Bay and Boca de Quadra. The relative downward mobility of ^{137}Cs with respect to $^{239,240}Pu$ (another fallout isotope) has been observed in the laboratory (Sholkovitz et al., 1983), in artificial microcosm tanks (Santschi et al.,1983) and in the field (Sholkovitz and Mann, 1984; Beasley et al., 1982). Edgington (1981) attributes the preferential downward transport of ^{137}Cs over $^{239,240}Pu$ to different adsorption affinities and diffusion coefficients. Beasley et al. (1982) suggest that particle mixing is responsible for the observed deeper ^{137}Cs and $^{239,240}Pu$ penetrations than expected from ^{210}Pb-derived sedimentation and mixing rates.

Santschi et al. (1983) attribute the mobility of ^{137}Cs over ^{210}Pb and $^{239,240}Pu$ to the less particle reactive properties of Cs. Sholkovitz et al. (1983) suggest that because of ion exchange reactions ^{137}Cs may increase in pore waters leading to downward and upward diffusive transport. Sholkovitz and Mann (1984) observe that a broad maximum in pore water activities of ^{137}Cs extends downward through a zone of sharply declining activity of ^{137}Cs in the solid phase, suggesting that ^{137}Cs is mixing downward in the pore waters faster than it is being taken up by sediments. However, although high porosities in the basin sediments of Smeaton Bay and Boca de Quadra should facilitate ^{137}Cs mobility in the sediments, mobility of ^{137}Cs is not observed in these fjord sediments.

Comparisons with Other Coastal Environments

Because this geochronology study of Smeaton Bay and Boca de Quadra represents the most comprehensive examination of sedimentation in Alaskan fjords, it is instructive to compare my results with those from other coastal environments (Table 3). Mean ^{210}Pb-sedimentation rates in Smeaton Bay and Boca de Quadra are roughly comparable with those found in other coastal areas of similar water depth. However, the ^{210}Pb inventories and fluxes in my study area are less than those found everywhere except on the Bering Sea shelf, and ^{137}Cs inventories are higher than most studied locations. This suggests that terrestrial inputs of sediment dominate the sediment loading to these fjords. At the time of this study, the watershed areas of Smeaton Bay and Boca de Quadra were totally undisturbed by man, but future

Table 3. Comparison of ^{210}Pb and ^{137}Cs distributions in sediments

Location	Lat. N°	Water depth m	^{210}Pb Excess surface activity dpm g^{-1}	^{210}Pb Mean sediment accumulation rate cm yr^{-1}	^{210}Pb Mean sediment accumulation rate mg $cm^{-2}yr^{-1}$	^{210}Pb Inventory dpm cm^{-2}	^{210}Pb Flux dpm $cm^{-2}yr^{-1}$	^{137}Cs Inventory mCi km^{-2}	^{137}Cs Penetration depth cm	Ref.
Wilson Arm, AK	55°	147±18 (n=3)	9.0±2.2	0.15±0.06	73±24	35.3± 6.1	1.10±0.19	30.0±16.7	16.4±5.5	1
Smeaton Bay, AK	55°	251±9 (n=3)	15.6±1.8	0.33±0.07	94±16	48.8± 5.7	1.52±0.18	18.1± 3.3	13.7±1.8	1
Boca de Quadra, AK	55°	322±66[a] (n=2)	17.0±5.4	0.38±0.12	76±19	44.8±13.9	1.40±0.43		13.8 (n=1)	1
		151±8[b] (n=2)	6.2±0.9	0.16±0.13	89±68	36.2± 5.9	1.13±0.18			
Marten Arm, AK	55°	186±19 (n=3)	4.7±4.0 (n=3)	0.15±0.16 (n=2)	57±48	36.8±13.6	1.14±0.42	29.1±12.3 (n=2)	10.6±3.3 (n=2)	1
Washington Coast	46-47°	canyon (n=32)	100±49		220±230		18±13			2
		slope (n=23)	110±48		53±25		5.2±3.1			
		shelf (n=85)	18±12		330±170		4.8±1.8			
Cape Lookout Bight, NC	34°	8 (n=4)		10.3±1.7	4130±670		>33.5	226	238	3
Hudson Shelf Valley, NY	40°	54±21 (n=5)	6.6±2.7		420±60	111.8±22.8	3.47±0.71			4
Saguenay Fjord, Quebec	48°	40	5.0		4000±800		20.0			5
		208±64 (n=7)	11.5±1.6		190±80		2.12±0.73		9.5±5.3 (n=3)	
Washington Continental Shelf	46-47°	105±21 (n=5)	5-100	0.36±0.08		187.6±45.5	5.83±1.41	43.2±14.6	19.8±1.8	6
Bering Sea Shelf	55°	142±4 (n=2)	5.9±0.8		80±10		0.54±0.06			7

Buzzards Bay, MA	41° 41°	16 16±1 (n=10)		0.30	
Wilkinson Basin, Atlantic continental shelf	42-43°	242±22 (n=6)			
NW Atlantic slope	40°	1300±692 (n=3)			
Saanich Inlet, B.C.	48°	228 210±14 (n=2),	13.4 14.4±0.4	0.8	130 180±120
Puget Sound, WA	47-49°		86±45		

[a] Basin
[b] Shallow

References:

1 - This study
2 - Carpenter *et al.* (1981)
3 - Chanton *et al.* (1983)
4 - Benninger and Krishnaswami (1981)
5 - Smith and Walton (1980)
6 - Beasley *et al.* (1982)
7 - Banahan (1983)
8 - Farrington *et al.* (1977)
9 - Sholkovitz and Mann (1984)
10 - Livingston and Bowen (1979)
11 - Bruland (1974)
12 - Matsumoto and Wong (1977)
13 - Carpenter *et al.* (1984)

	14.2	40	8,9
	7.1±3.1		10
	2.8±1.0		
	3.9±2.7		
2.1			11
3.5±2.3			12
			13

agricultural, logging, and mining operations will inevitably further increase the terrestrial contribution to the sediments of these fjords.

SUMMARY AND POSSIBLE CONSEQUENCES

Although in fjords such as the two studied here, ^{210}Pb and ^{137}Cs geochronologies are affected by riverine input, non-steady state deposition of sediment, frequent slumping due to the steep topography, and regional variation in the available organic and inorganic particulate phases present, a range of time-averaged sedimentation rates can be obtained. Most of the ^{137}Cs observed in the sediments is terrestrial in origin and is delivered to the fjords after some unknown, but probably short lag period; the more particle-reactive ^{210}Pb is primarily of marine origin. Intense mixing is responsible for the deep ^{137}Cs penetration in the river-dominated, shallower stations, and obscures the smaller peak of ^{137}Cs arising from fallout directly on the fjord surface. At the deep basin stations, the mixing rate is insufficient to cause a significant SML in the ^{210}Pb profiles, as observed at shallower stations. Episodic physical mixing, documented by vertical distributions of trace metals and radioisotopes, does not necessarily preclude use of simplified mixing models as long as sedimentation rates are relatively high and ancilliary data is available to verify assumed mixing processes.

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4. Spatial and Temporal Patterns of Chemical Diagenesis in Sediments of Smeaton Bay and Boca de Quadra, Alaska

Abstract- Spatial and temporal influences upon trace metal and nutrient distributions in interstitial water were examined in two pristine fjords where bottom water temperatures seasonally vary less than 1°C. Over a three-year period, interstitial Mn, Fe, ammonia, and phosphate were examined in sediment from five stations in the basins and shallower areas of Smeaton Bay and Boca de Quadra, southeast Alaska. Episodic physical mixing and the supply of reactive (autochthonous) organic matter are responsible for the temporal variations observed. Incidents of sediment slumping are most frequent at shallower (127 -152 m) stations where interstitial waters show considerable small scale variability, and are greatly undersaturated with respect to Mn- and Fe- carbonate or phosphate solids. In contrast, reducing conditions in sediments from the main basin of Boca de Quadra result in large fluxes of Mn^{2+}, which appears to be in equilibrium with rhodochrosite or similar Mn carbonate. Sediment from the main basin of Smeaton Bay is intermediate between these two extremes.

INTRODUCTION

The flux of reactive solutes from the sediment-water interface is of particular importance in estuaries where the benthic nutrient flux may be more important than rivers in supplying nutrients to the water column. In addition, river-supplied heavy metals and organics (both natural and anthropogenic) are stored in estuarine sediments where

they may be remobilized or permanently buried. Thus, knowing the fate of trace metals and nutrients within nearshore sediments is critical not only to estuarine geochemical cycles, but also to oceanic mass balances of these components. Nutrient and trace metal fluxes have been estimated from interstitial water profiles and/or measured directly in chamber experiments from a number of different locations, most notably Long Island Sound (Aller, 1980, Aller and Benninger, 1981), Narragansett Bay (Elderfield et al, 1981), Cape Lookout Bight (Klump and Martens, 1981), and Great Bay Estuary, New Hampshire (Hines et al, 1982). These studies, conducted at relatively shallow depths, have indicated a strong seasonal influence on benthic fluxes arising from temperature changes in the bottom waters and sediments. At some of these sites, seasonal and spatial variations in natural fluxes are complicated by significant anthropogenic inputs. The present study was conducted to examine spatial and temporal influences upon benthic nutrient and trace metal fluxes from a pristine fjord where bottom water temperatures seasonally vary less than 1°C. This chapter describes interstitial water profiles from cores collected on 20 cruises over a 3 yr period and discusses the relative importance of physical and chemical processes in determining the sedimentary fluxes of N, P, Fe, and Mn from Smeaton Bay and Boca de Quadra, southeast Alaska.

STUDY AREA

Five stations in Smeaton Bay and Boca de Quadra have been chosen for detailed study: WA2 and WA1 in Wilson Arm, SB0 and SB1 in Smeaton Bay, and BQ9 in the central basin of Boca de Quadra. The location,

description and geochronology of these stations are given in Chapter 3 and will be only briefly summarized here. WA2 and WA1 are relatively shallow (127 and 152 m, respectively) stations that lie approximately 3 and 6 km from the Wilson-Blossom River, and sediments from these stations are subject to deep physical mixing. SB0 and SB1 are stations in the 240-250 m deep basin of Smeaton Bay, and BQ9 is in the 370 m central basin of Boca de Quadra.

METHODS AND MATERIALS

Sampling Methods

The sediment and interstitial water samples were collected using a Benthos gravity corer with 6.7 cm i.d. plastic core liners without core catcher, nose cone, or pipe barrel. Cores collected for %C and %N were sectioned immediately and frozen for later analysis. Cores collected for interstitial water were extruded directly into PVC Reeburgh (1967) squeezers constructed with i.d. virtually identical to that of the core liner thereby minimizing atmospheric exposure. Interstitial water was squeezed from the sediment using 5-30 psi of ultrapure nitrogen gas at reduced temperatures. Two precombusted Whatman EPM 1000 filters were used in the squeezers. The initial several mL of interstitital water removed from each section was discarded. Samples from nutrients were collected in conventional polyethylene bottles and frozen. Samples for Fe and Mn were collected in acid-washed LPE bottles, acidified with ultrex HCl and stored frozen.

Analytical Techniques

Sediment C and N was determined by combustion in a Perkin-Elmer model 240C CHN analyzer. Total C levels can be considered to be organic C since carbonate C levels are less than 3 mg g^{-1} in these sediments. Total Fe, Mn, and Cu were determined by flame atomic absorption following $LiBO_2$ fusion (Medlin et al., 1969)

Dissolved inorganic nutrients were determined by autoanalyzer. For ammonia, the method used was that of Koroleff (1970). Nitrite was determined by the Greiss reaction, as described by Armstrong et al. (1967). Nitrate is quantitatively reduced to nitrite using copperized Cd filings. The inorganic phosphate procedure used was that of Murphy and Riley (1962)

Interstitial Fe was analyzed using the ferrozine technique of Stookey (1970) as applied to natural waters by Murray and Gill (1978) and Gibbs (1979) Interstitial Mn was determined by direct injections of 1:100 dilutions of interstitial water samples into a Perkin-Elmer model 360 atomic absorption spectrophotometer with HGA 2100 furnace.

RESULTS

Wilson Area

Mn and Fe profiles in interstitial water from station WA2, approximately 3 km from the Wilson-Blossom River outfall, are shown in Fig. 1 and listed in Appendix C. On only one occasion (October 1980) does the pore water Mn curve indicate a steady state reaction profile typical of sediments from areas with high sedimentation rates.

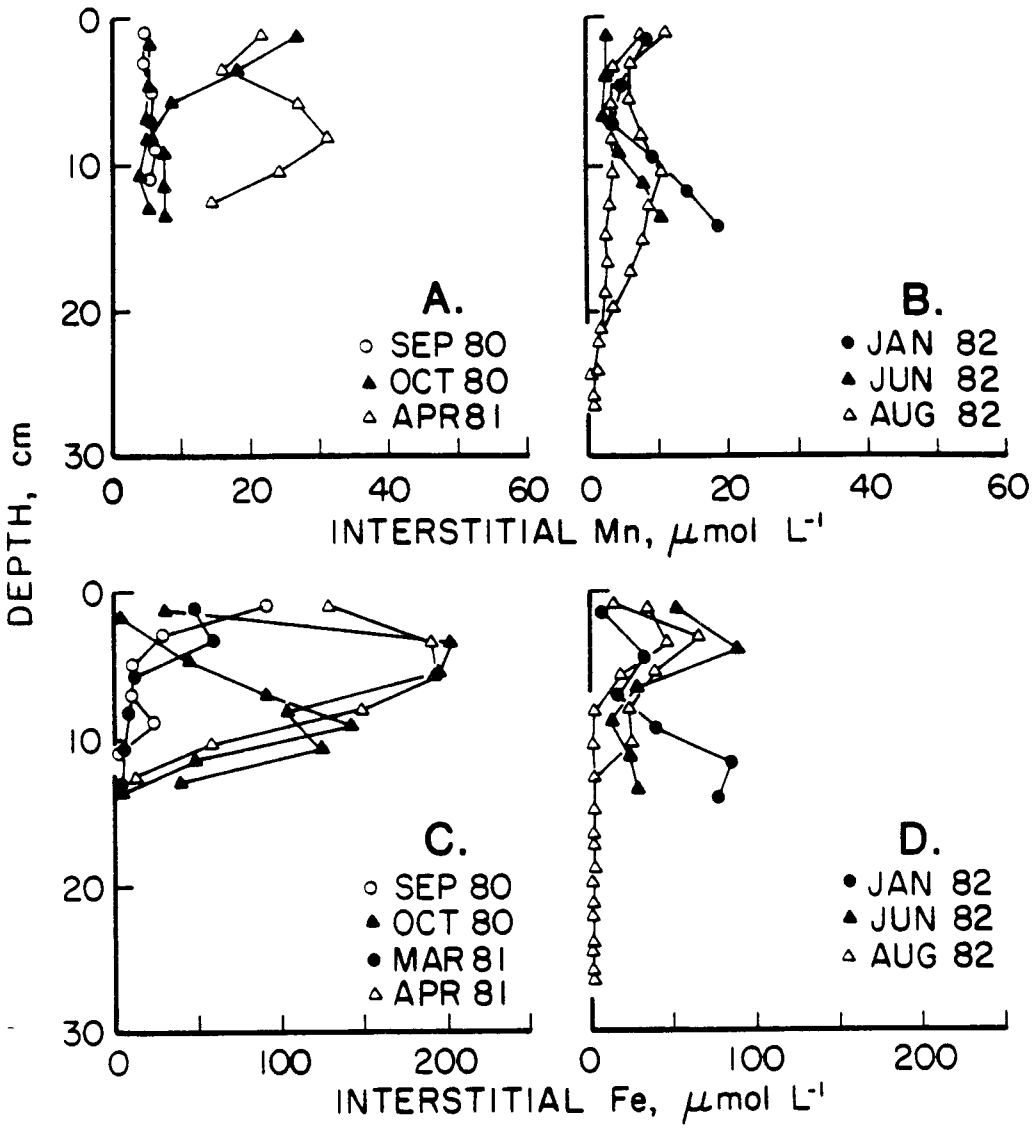


Fig. 2. a. Interstitial Mn vs. depth at station WA2, 1980-1981.
b. Interstitial Mn vs. depth, 1982.
c. Interstitial Fe vs. depth, 1980-1981.
d. Interstitial Fe vs. depth, 1982.

Generally, the pore water Fe curves exhibit large subsurface maxima that seasonally vary in depth and magnitude. Interstitial ammonia and phosphate profiles at WA2 are characterized by large differences between cruises and significant variation between two cores collected in December 1980 (Fig. 2). Nitrate and nitrite concentrations are generally low except in the surficial sediment sections (Appendix D).

Interstitial water profiles for Mn at station WA1 (Fig. 3) are more variable in shape than those at WA2; however, subsurface peaks in Fe occur less frequently and are smaller in magnitude than those for the station 3 km closer to the Wilson-Blossom River. Ammonia and phosphate concentrations (Fig. 4) in the interstitial water are less variable and lower than those at WA2. In November 1979, April 1980, and June 1980, the ammonia profiles seem to be approaching an asymptotic value, and the Mn and Fe concentrations are generally low, with the highest levels at the sediment-water interface. By September 1980, a subsurface Fe peak has developed and ammonia levels are reduced. In October 1980, the subsurface Fe peak has reached 165 umol L^{-1} with sharp gradients in both directions. Detectable Mn is observed throughout the core. In March 1981, the ammonia values are extremely low; the Fe and phosphate profiles exhibit broad, subsurface peaks. One month later, in April 1981, the Fe and phosphate peaks have diminished and ammonia levels have increased. The August 1981 profiles of Fe, Mn, phosphate, and ammonia are similar in form to those from September 1980.

Sweaton Bay Basin

Cores were collected at station SB0 at less frequent intervals

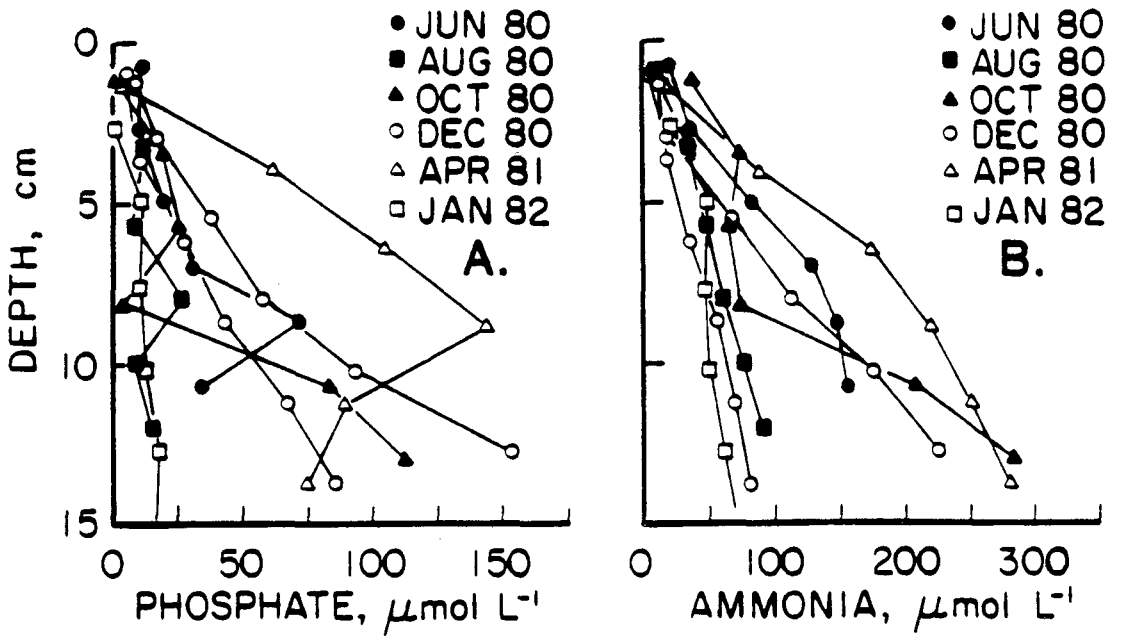


Fig. 2. a. Interstitial phosphate vs. depth at station WA2.
b. Interstitial ammonia vs. depth.

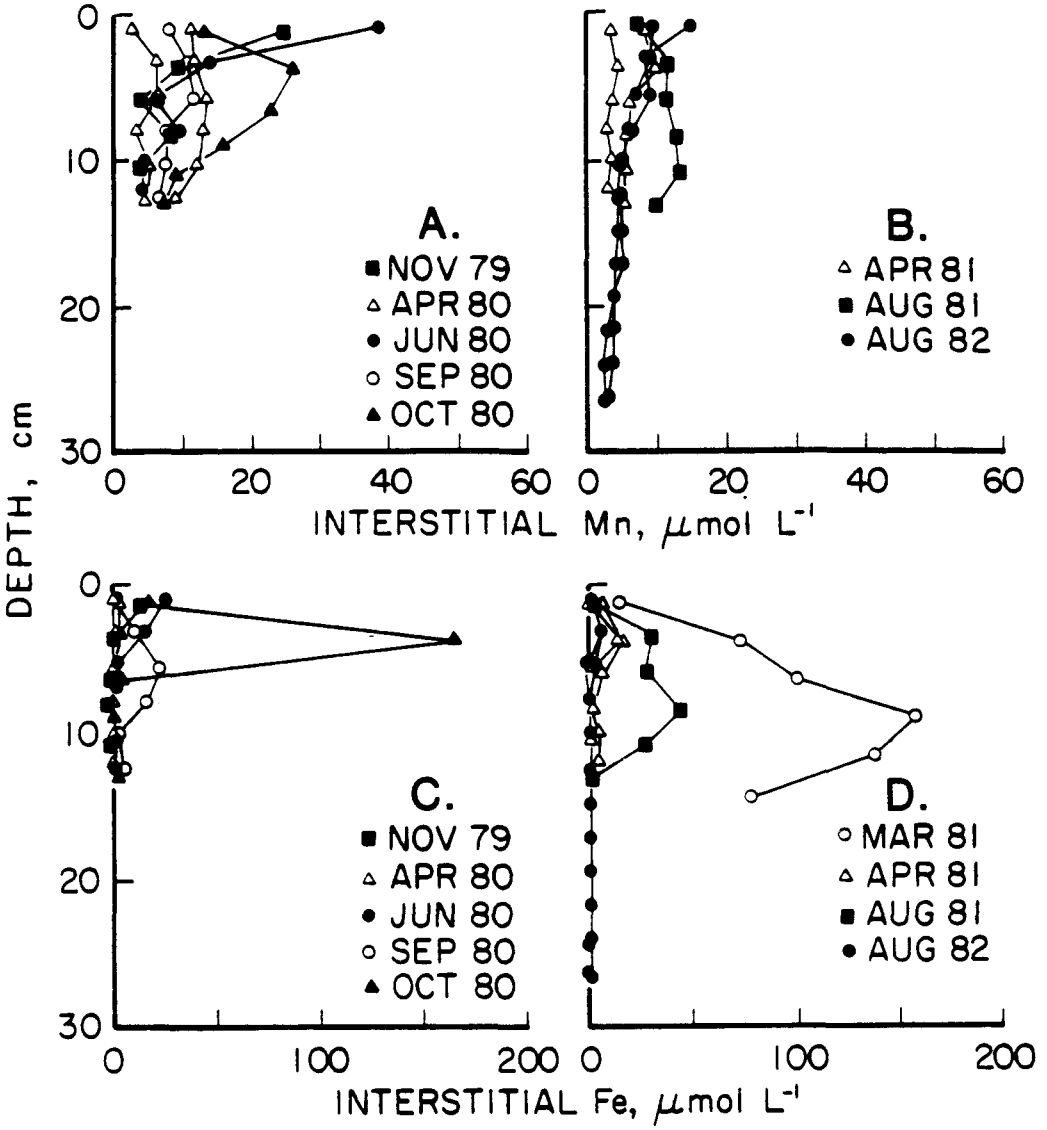


Fig. 3. a. Interstitial Mn vs. depth at station WA1, 1979-1980.
b. Interstitial Mn vs. depth, 1981-1982.
c. Interstitial Fe vs. depth, 1979-1980.
d. Interstitial Fe vs. depth, 1981-1982.

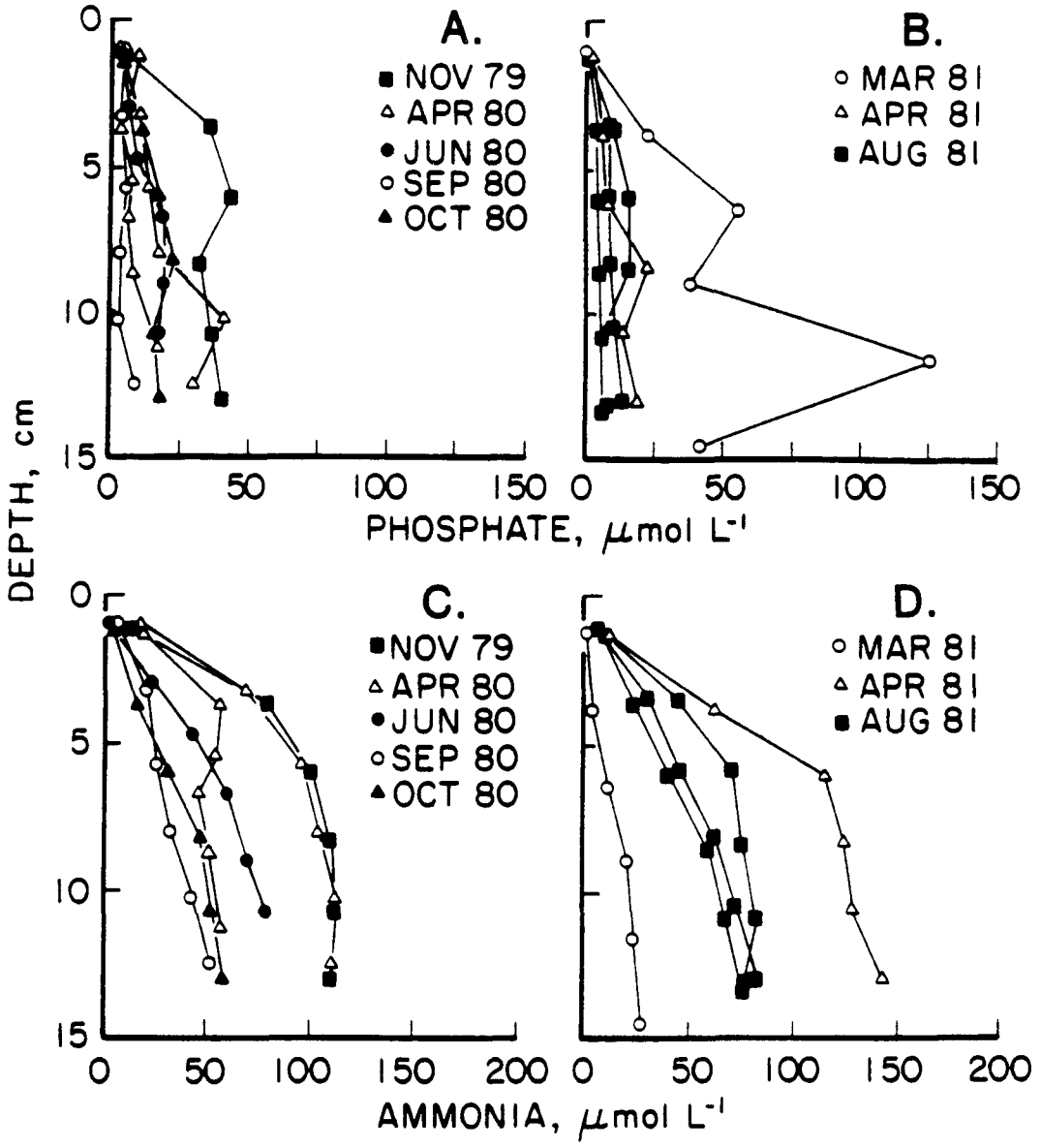


Fig. 4. a. Interstitial phosphate vs. depth at station WA1, 1979-1980.
b. Interstitial phosphate vs. depth, 1981.
c. Interstitial ammonia vs. depth, 1979-1980.
d. Interstitial ammonia vs. depth, 1981.

than at WA1. Interstitial Mn and Fe profiles are shown in Fig. 5 and nutrients in Fig. 6. As at station WA1, the interstitial Fe has a strong subsurface peak in March 1981 that is repeated in April 1982 (a time when WA1 was not sampled). In August 1982, there is a large surface peak in Fe and a smaller peak in Mn. At all three sampling times (June 1980, December 1980, and August 1982), none of the ammonia profiles approaches an asymptotic value but are increasing with depth.

Fig. 7 shows the profiles for interstitial Mn and Fe at station SB1. Subsurface Mn peaks occur at three times: March 1981, January 1982, and April 1982. Although there is considerable variation between duplicate cores, the Fe concentrations reach high levels in March 1981 as observed at stations WA1 and SB0. Like WA1, by June 1981, the sub-surface peak has decreased and in August and September 1981, Fe levels are low. In 1982, subsurface Fe concentrations are high in January and April. The later profile was also observed at SB0. Nutrient profiles (Fig. 8) show that small scale horizontal variability in the ammonia concentrations are as great as seasonal variations. As observed at WA1, the ammonia concentrations are extremely low in March 1981 (less than 18 umol L^{-1}) throughout the core. Phosphate concentrations are less than 25 umol L^{-1} at all times sampled and vary little with depth.

Temporal variations at SB1 are also seen in the solid phase. Fig. 9 shows the sediment profiles for total Mn and Cu in March 1981, June 1981 and August 1982. The sediment Cu profile in March 1981 is virtually constant with depth but has a subsurface peak in June 1981 and August 1982.

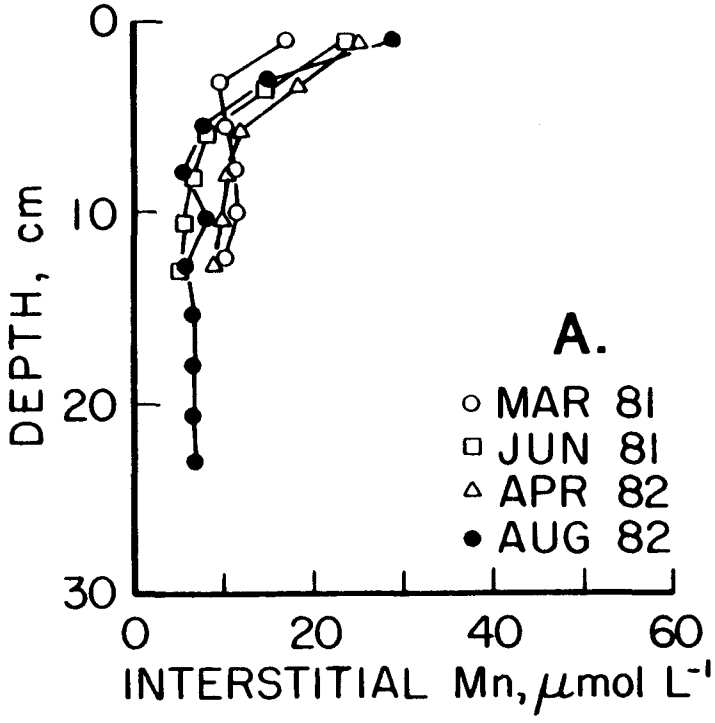
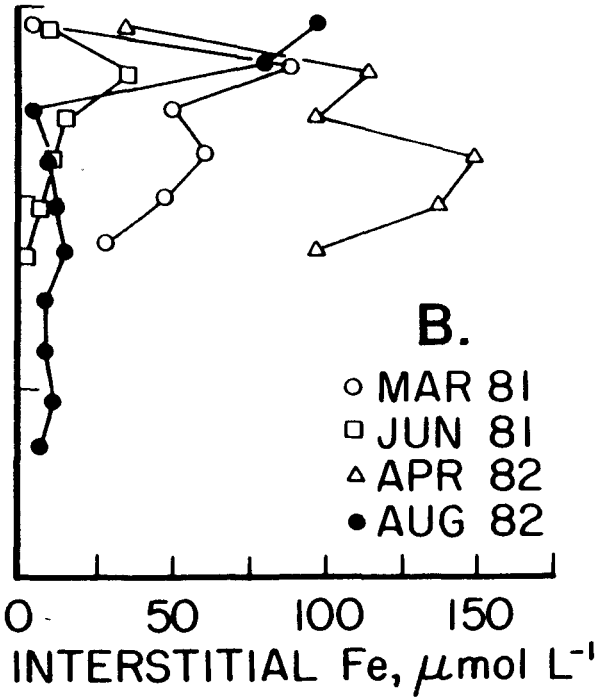


Fig. 5. a. Interstitial Mn vs. depth at station SBO.
b. Interstitial Fe vs. depth.


B.
MAR 81
JUN 81
APR 82
AUG 82
0
50
100
150
INTERSTITIAL Fe, μmol L⁻¹

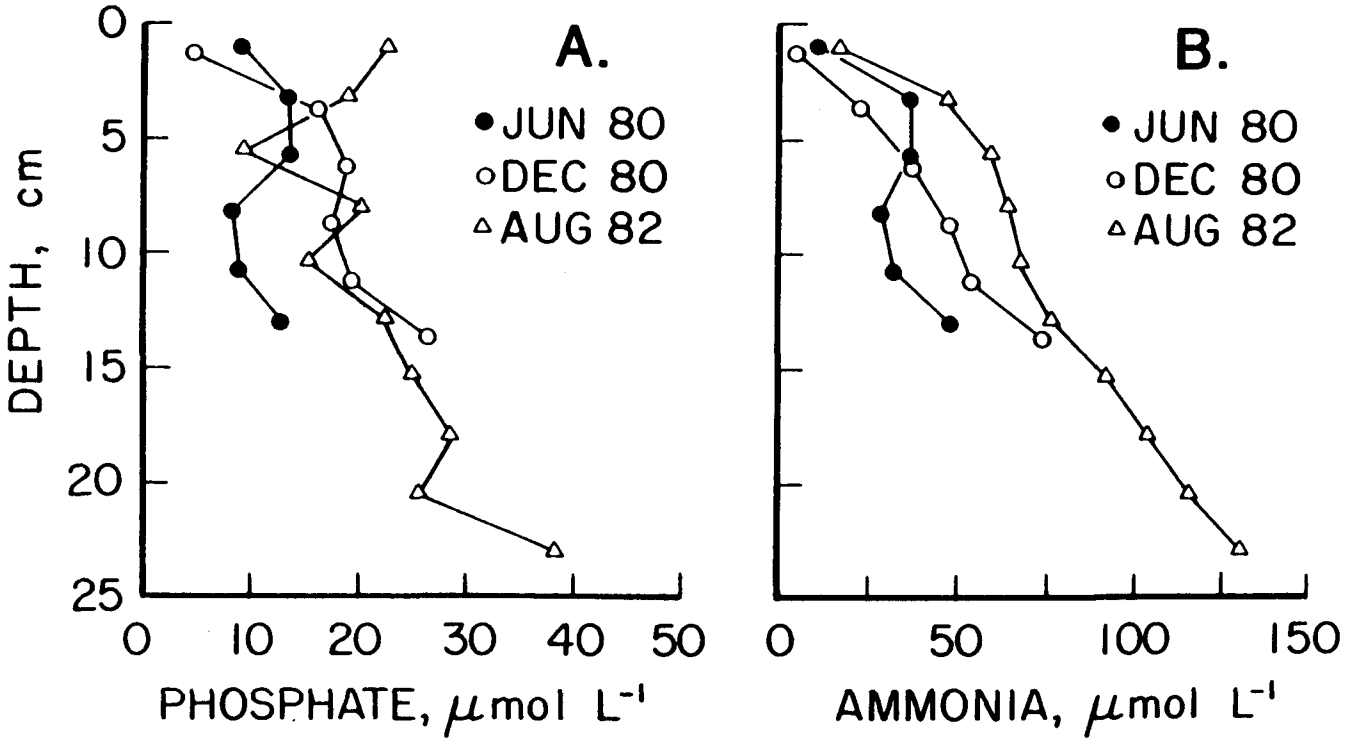


Fig. 6. a. Interstitial phosphate vs. depth at station SB0.
b. Interstitial ammonia vs. depth.

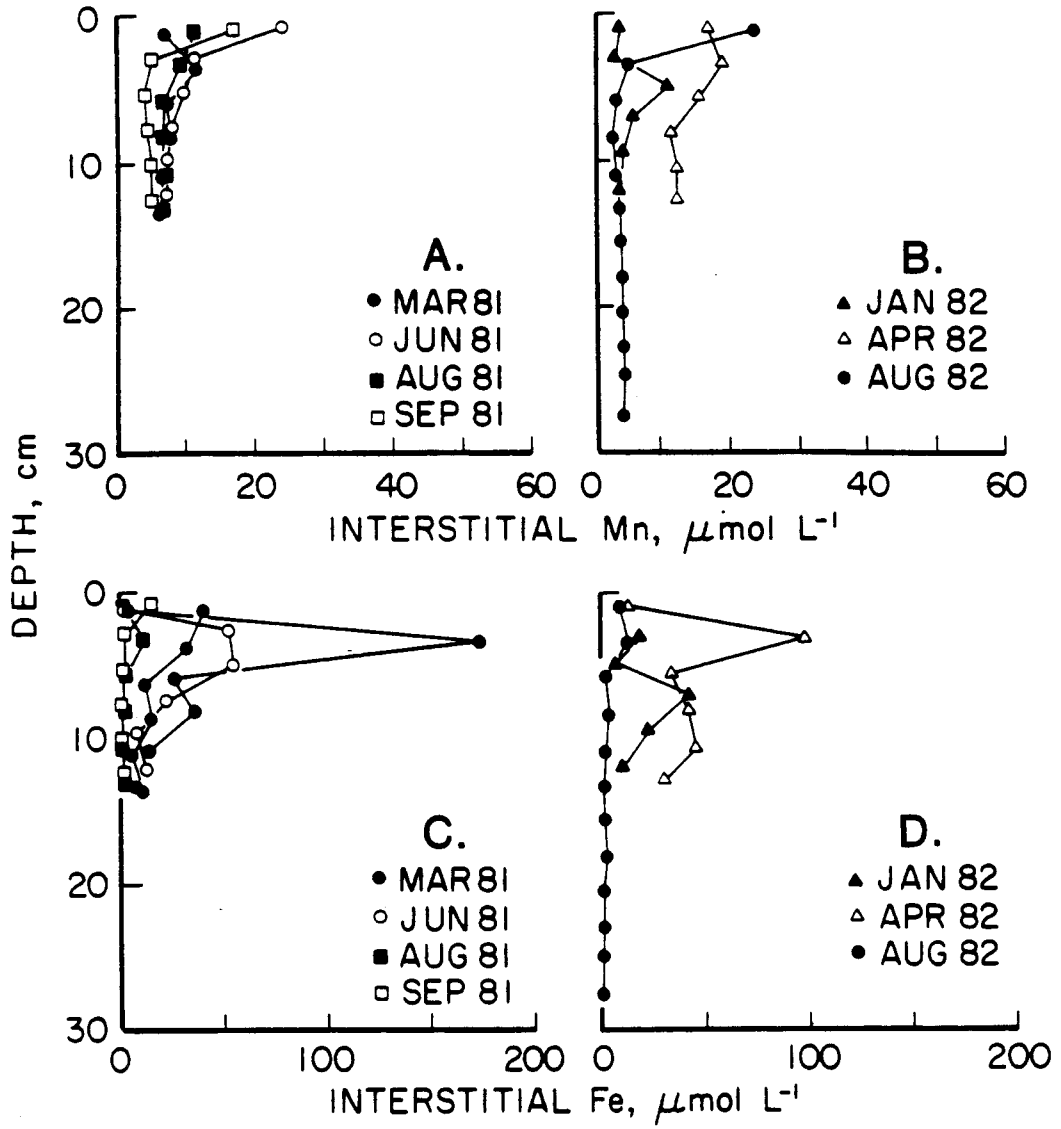


Fig. 7. a. Interstitial Mn vs. depth at station SB1, 1981.
b. Interstitial Mn vs. depth, 1982.
c. Interstitial Fe vs. depth, 1981.
d. Interstitial Fe vs. depth, 1982.

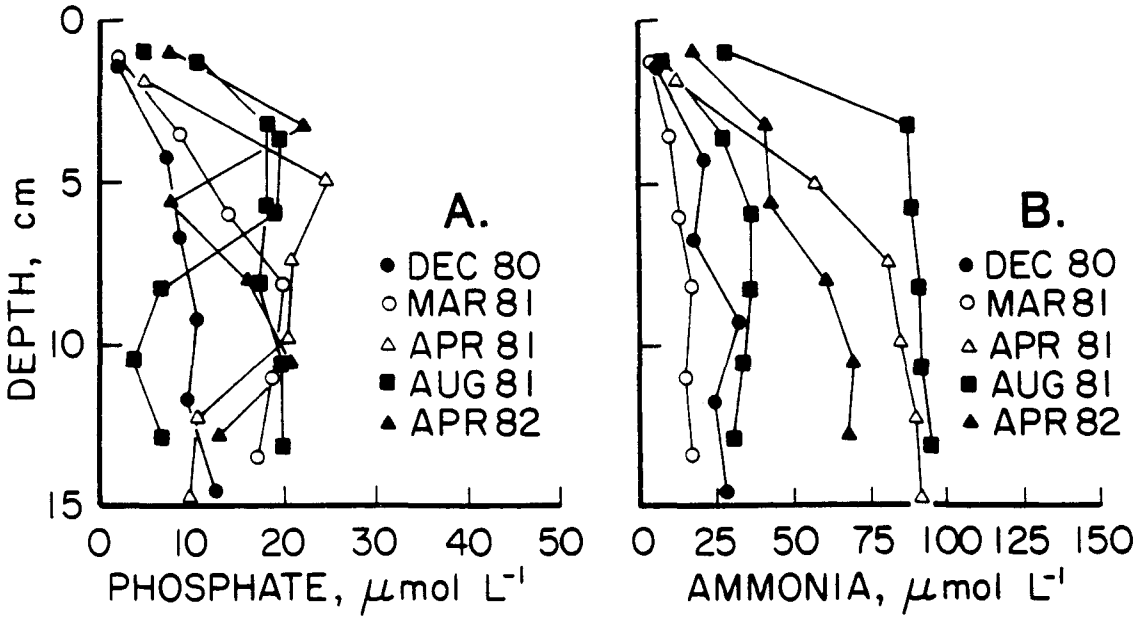


Fig. 8. a. Interstitial phosphate vs. depth at station SB1.
b. Interstitial ammonia vs. depth.

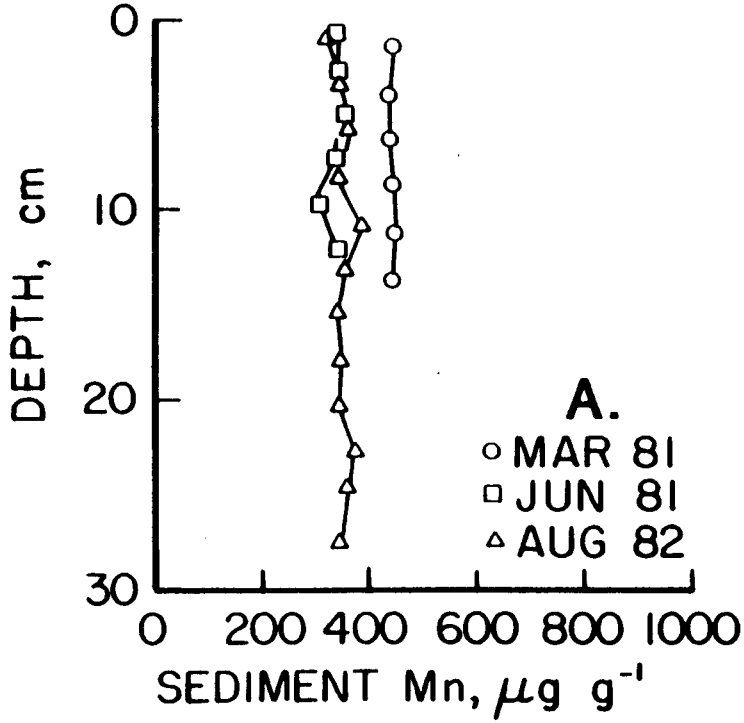
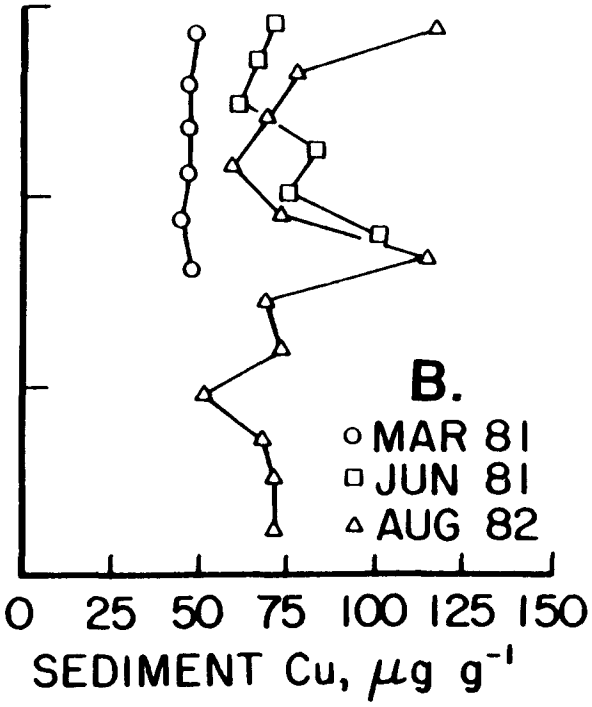


Fig. 9. a. Total sediment Mn vs. depth at station SB1.
b. Total sediment Cu vs. depth.


B.
MAR 81
JUN 81
AUG 82
0 25 50 75 100 125 150
SEDIMENT Cu, μg g⁻¹

Main Basin of Boca de Quadra

Pore water profiles for Mn and Fe at station BQ9 are shown in Fig. 10. Mn concentrations are highest in the surficial sediments and are considerably higher than at any other station sampled. All the Fe curves reach a subsurface maxima and become undetectable below approximately 6 cm depth. The highest Fe concentrations are observed in August and September 1980. With the exception of the core collected in June 1980, all the phosphate profiles have subsurface maxima (Fig. 11). Generally, the ammonia curves seem to be approaching an asymptotic value at depth except in August and September 1981.

DISCUSSION

General Patterns of Seasonal and Spatial Variation in Pore Water Profiles

Seasonal patterns in pore-water profiles from Smeaton Bay and Boca de Quadra are difficult to discern because they are complicated by small scale horizontal variability and episodic events. Unlike bioturbation and bioirrigation which tend to homogenize interstitial water profiles but do not change the total inventory of solid phase tracers like ^{210}Pb, physical slumping and mixing can actively transport sediment from one location to another. Therefore, a time-series of interstitial water profiles from a given station in Smeaton Bay or Boca de Quadra may represent conditions where the solid phase is not constant. A conceptual analogy may be made with fluid

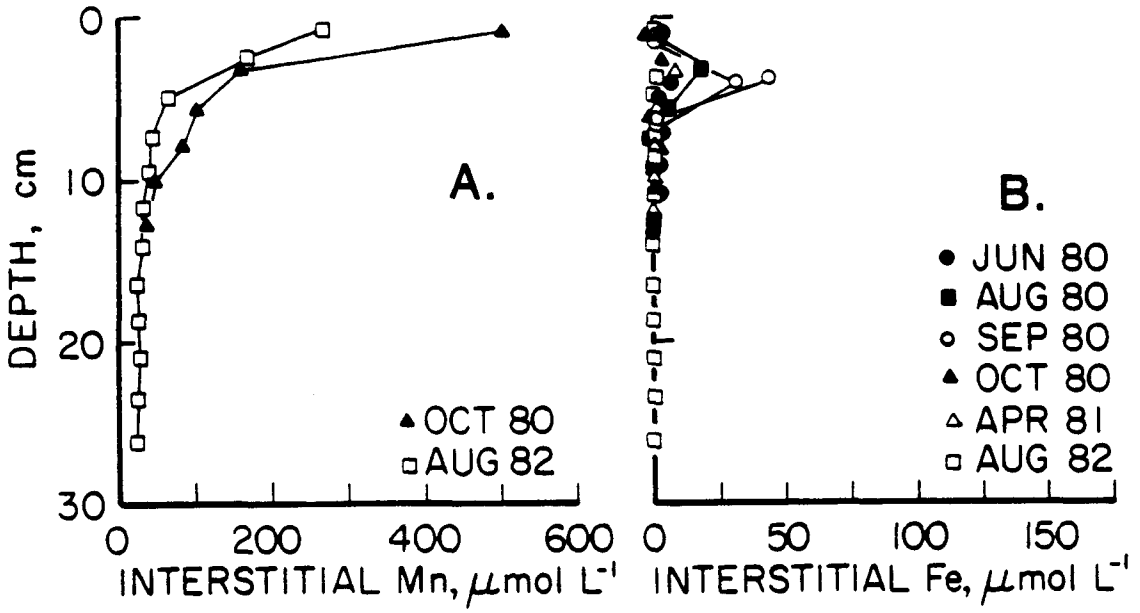


Fig. 10. a. Interstitial Mn vs. depth at station BQ9.
b. Interstitial Fe vs. depth.

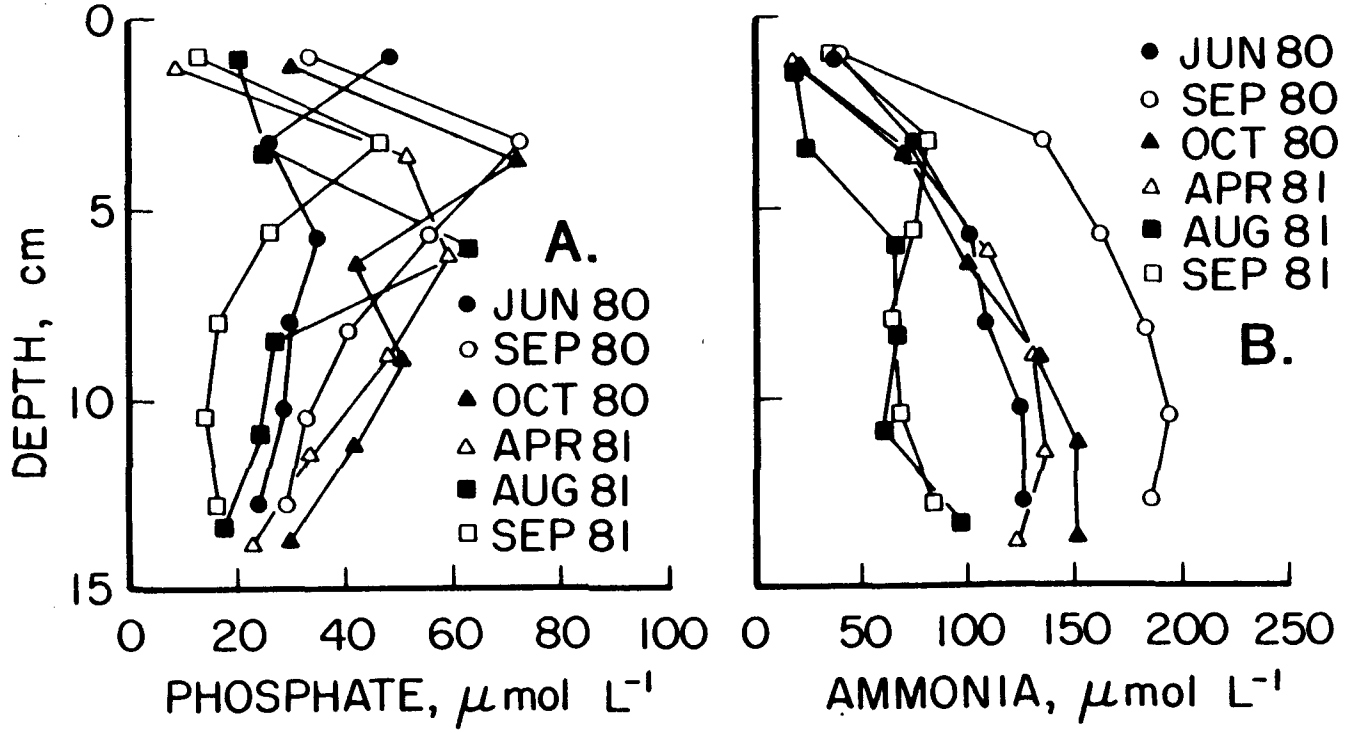


Fig. 11. a. Interstitial phosphate vs. depth at station BQ9.
b. Interstitial ammonia vs. depth.

dynamics. Most sediment studies involve movement by bioturbation, and are Lagrangian in nature. That is, like a drifting buoy, these studies describe motion in a fixed element and regard parameters (T, S°/oo, concentration, velocity) as a function of that element and time. In the case of the buoy, the motion is in the horizontal direction and the water parcel remains constant, while for the bioturbated sediment the motion is in the vertical direction with the total sediment column below a given area remaining unchanged. In a dynamic fjord like Smeaton Bay, the time series pore water profiles describe an Eulerian system, a crude sediment analogy to a moored current meter, where we regard the concentrations as a function of a fixed position in space (latitude, longitude, distance from physical markers) which we follow in time. However, unlike a current meter which frequently records velocities (giving speeds and direction of movement), our sediment sampler gives only concentrations at infrequent intervals from which we must extrapolate and speculate. The limitations of our time series record obtained by discrete coring and removing interstitial water by squeezing are: (1) sediment movement is irratic, often limited in extent, and may originate from the watershed or another location within the fjord, (2) sampling intervals are likely to be insufficient to record all the major events occurring at dynamic locations, especially near river outfalls, (3) shipboard station positioning is not precise enough to eliminate small scale spatial variability in cores collected at the same time, and (4) using squeezers to process sediment integrates concentration gradients occurring over several cms of depth, effectively removing vertical

fine structure. In particular, the gradients of solutes at the sediment-water interface will be strongly dependent upon how carefully the flocculent surface layer is retrieved. Having outlined the limitations placed upon our approach, we will attempt to determine likely processes responsible for observed interstitial water distributions.

a) Wilson Arm

Interstitial water profiles at WA2, the station closest to the Wilson-Blossom River outfall, show the greatest seasonal and small scale spatial (between cores collected on the same cruise) variation. Phosphate and ammonia concentrations are considerably higher at this station than at WA1, the other relatively shallow station in Wilson Arm. One plausible explanation for this observation is that because WA2 is closest to the river outfall, it receives significantly more N- and P-rich particulate matter associated with salmon spawning in August. However, there are no distinct seasonal increases in these nutrient species in interstitial water that can be attributed to salmon, as have been observed in the river water (Sugai and Burrell, 1984). This may be because the fall storms that are responsible for much of the deep mixing at river-dominated stations (Chapter 3), occur soon after the reactive fish debris is deposited. This riverine mixing is likely responsible for the large variation observed in "duplicate" cores collected in October 1980 (Figs. 1a, 1b), December 1980 (Figs. 2a, 2b), and August 1982 (Figs. 1c, 1d). While the general shapes are similar for all profiles except the Mn distributions in October 1980, the range of concentrations obtained

from sediment inhomogeneity is in some instances as great as the seasonal variation. Elderfield et al. (1981) observed similar "patchiness" in interstitial water profiles from Narragansett Bay which they attributed to infauna population differences over small areas.

The interstitial water profiles for Mn, Fe, and ammonia at station WA1 suggest a site influenced by several events during the three years sampled, but one in which solute exchange between sediment and overlying water at times may be described by a diffusive flux. Small scale variation between cores collected during the same cruise (Figs. 3 and 4) are generally less than at WA2, the station closer to the river. In August 1982, a 10-cm long worm tube was observed in one of the cores collected for Fe and Mn, but as seen in Figs. 3b and 3d, the resulting variation between duplicate cores is minimal.

b) Smeaton Bay

The Mn profiles for interstitial water from the main basin of Smeaton Bay (stations SB0, SB1) suggest that during relatively quiescent periods between sediment slumps (Chapter 3), the flux of Mn from the sediment-water interface is controlled by the availability of labile organic matter. Although our sampling interval precludes determining a direct relationship between recent primary productivity in the overlying water and calculated Mn fluxes from the sediment, our data suggest that estimates of the diffusive Mn fluxes resulting from interstitial water profiles are highest in the summer (June 1981, August 1982). Uncertainties in predicting solute fluxes from

interstitial water profiles are large (especially in the possible presence of non-diffusive mechanisms enhancing transport), and significant errors can result from disturbance of the high porosity surface layer during coring, choice of diffusion coefficient, and insufficient data near the sediment-water interface. However, diffusive flux estimates can indicate relative conditions, which are the objective here. Sediment-water flux estimates for Mn at station SB1 (Table 1) were calculated using the expression (Berner, 1971)

$$J = - \phi D_s \left(\frac{\partial c}{\partial z}\right)$$

where: J = flux from sediment to overlying water, umol $cm^{-2}s^{-1}$

ϕ = sediment porosity at interface

D_s = bulk sediment diffusion coefficient at interface, taken to equal 3.65×10^{-6} cm^2s^{-1} at 4°C (Aller, 1980)

$\left(\frac{\partial c}{\partial z}\right)$ = pore water concentration gradient at sediment-water interface, umol cm^{-4}

Our results agree with the findings of Hunt (1983) from mesocosm studies in Narragansett Bay. Hunt (1983) found that during summer, the Mn flux was strongly correlated not to temperature, but to the average primary productivity during the month preceding the flux determination. This is in contrast to studies in Buzzards Bay, Massachusetts (Sholkovitz and Mann, 1984) and Long Island Sound (Aller and Benninger, 1981) that suggest that temperature dependence of the dissolution reaction is primarily responsible for the seasonal variation in fluxes. Elderfield et al. (1981) suggest that temporal variation in interstitial water profiles is most likely when bioturbation rates are low and the competing effects of physical

Table 1.

Diffusive Mn Fluxes Calculated From Pore Water Profiles

at Smeaton Bay Basin Station, SB1

Date Collected	Mn concentration umol L^{-1}	J umol $cm^{-2}s^{-1}$
March 1981	7.14	3.03×10^{-8}
June 1981	24.3	11.0×10^{-8}
August 1981	11.6	3.94×10^{-8}
September 1981	17.2	6.87×10^{-8}
January 1982	4.6	1.56×10^{-8}
August 1982	23.9	7.73×10^{-8}

(bioturbation) and chemical (metabolism) activity are more delicately balanced; conditions believed to exist in Smeaton Bay during non-disturbed periods.

Large sub-surface increases in interstitial Fe (Figs. 5b, 7c, 7d) are observed in winter and early spring (March 1981, January 1982, April 1982) and likely represent an abiogenic oxidation of Fe-sulfides occurring during times of enhanced physical mixing. As suggested by Aller (1980), because the oxidation of Fe-sulfides is rapid, the release might be best conceptualized as a colloid flux. Colloids of Fe-oxides would easily pass through the glass fiber filters used in sediment processing, and would operationally be included in the pool of "dissolved" interstitial Fe. Winter profiles for ammonia (Fig. 8b) at SB1 are consistent with the hypothesis of physical mixing in winter. Decreased ammonia concentrations suggest that the diagenesis of organic matter has been interupted with resultant removal of ammonia from the interstitial water to the overlying water.

c) Boca de Quadra

As seen in Chapter 3, station BQ9, in the main basin of Boca de Quadra, is not subject to the frequent mixing events observed in Smeaton Bay and other areas of Boca de Quadra. The interstitial Mn and Fe profiles (Fig. 10) indicate reducing conditions very near the sediment-water interface, and the resultant diffusive flux of Mn is 1.23×10^{-6} umol $cm^{-2}s^{-1}$ (38.7 umol $cm^{-2}yr^{-1}$). The diffusive Mn flux estimated from the interstitial water profile at BQ9 is high compared to other marine environments, especially when temperature effects are considered. Mn fluxes predicted from pore water profiles from the

Mississippi River delta range from 0.5 - 15 umol $cm^{-2}yr^{-1}$ (Trefry and Presley, 1982). Chamber experiments in Narrangansett Bay yield Mn fluxes of 7 - 18 umol $cm^{-2}yr^{-1}$ (McCaffrey et al., 1980). At 4°C in Long Island Sound (Aller, 1980), Mn fluxes estimated from pore water profiles (which were in all cases greater than those determined from direct measurements) ranged from 3 - 9 umol $cm^{-2}yr^{-1}$. As will be shown in the following section, Mn concentrations in the interstitial water of BQ9 appear to be controlled by saturation with rhodochrocite or similar Mn carbonates. The variability observed in the interstitial phosphate and ammonia profiles at station BQ9 probably represents small scale sediment inhomogeneity rather than seasonal differences.

Thermodynamic Control on Pore Water Concentrations

Thermodynamic calculations were made to determine whether the formation of authigenic minerals can control the solubility of Fe^{2+}, Mn^{2+}, and PO_4^{3-} in the sediments from Smeaton Bay and Boca de Quadra. The degree of saturation of interstitial water was estimated by comparing the ion activity product, IAP, of the ions in solution with the thermodynamic solubility product, K_{so}. This requires for an electrolyte, CA, where C is the cation, and A, the anion, that K_{so}, (which = $a_C a_A$), is known at a given temperature and pressure. The IAP was calculated from measured molalities (m_i) in the pore waters and the individual ion activity coefficients of the free ion $(\gamma_i)_F$ and of the free plus ion-paired ion $(\gamma_i)_T$ for a given temperature, pressure, and ionic strength, I. I was calculated from the expression:

$$I = 0.5 \left(\sum_i m_i z_i^2 \right)$$

where, z_i is the charge of ion i.

Ion activity products were calculated for siderite ($FeCO_3$), rhodochrosite ($MnCO_3$), vivianite ($Fe_3(PO_4)_2 8H_2O$), and reddingite ($Mn_3(PO_4)_2 3H_2O$) for cores from Wilson Arm (station WA1, 4/80 and 10/80) and Boca de Quadra (BQ9, 10/80) Total alkalinity was assumed equivalent to carbonate alkalinity. The reactions, solubility products, and references are given in Table 2.

The results of the calculations are plotted as -log IAP vs depth for station BQ9 in October 1980 and station WA1 in April and October 1980 (Fig. 12). The pore waters are saturated with respect to rhodochrosite in the surface sections of BQ9 suggesting that mixing is relatively infrequent at this station, in agreement with results from the ^{210}Pb and ^{137}Cs geochronologies. By contrast, interstitial waters at WA1 are undersaturated with respect to this Mn carbonate at all depths sampled both in April and October. Log Ω , the degree of saturation, where $\Omega = (IAP/K_{so})$, is -0.6 (slightly undersaturated) for the Fe carbonate, siderite, in the second section of the core collected in April 1980 at WA1 and becomes more negative both above and below this section. In October 1980, when interstitial water profiles suggest an active mixing event, log Ω = -1.5 for siderite. Vivianite and reddingite, the Fe and Mn phosphates are undersaturated at both stations by a factor of 10^3 or more.

SUMMARY

Temporal variations in interstitial water profiles from shallow and basin stations in Smeaton Bay indicate that episodic physical

Table 2. Solubility Products for Selected Iron and Manganese Solids

Reaction	-log K_{so}	T (^{o}C)	Reference
Siderite			
$FeCO_3 = Fe^{2+} + CO_3^{2-}$	10.4	5	Stumm and Morgan (1970)
Rhodochrosite			
$MnCO_3 = Mn^{2+} + CO_3^{2-}$	10.5	10	Robbins and Callendar (1975)
Vivianite			
$Fe_3(PO_4)_2 \cdot 8H_2O = 3Fe^{2+} + 2PO_4^{3-} + 8H_2O$	33.5	5	Tessenow (1974)
Reddingite			
$Mn_3(PO_4)_2 \cdot 3H_2O = 3Mn^{2+} + 2PO_4^{3-} + 3H_2O$	31.8	5	Tessenow (1974)

$(\gamma_{Fe^{2+}})_T = (\%\text{Free})(\gamma_{Fe^{2+}})_F = 2.99 \times 10^{-2}$

(%Fe free) = 13% at pH 7.5 (Kester et al., 1975)

$(\gamma_{Fe^{2+}})_F = 0.23$ (by analogy to Ca^{2+})

$(\gamma_{PO_4^{3-}})_T = (\%\text{Free})(\gamma_{PO_4^{3-}})_F = 3.3 \times 10^{-5}$

$(\%PO_4^{3-}\text{ free}) = 0.1\%$ (Atlas, 1975)

$(\gamma_{PO_4^{3-}})_F = 0.033$ (Atlas, 1975)

$$[PO_4^{3-}]_T = \frac{\text{(measured phosphate conc.)}}{\frac{[H^+]^3}{K_1K_2K_3} + \frac{[H^+]^2}{K_2K_3} + \frac{[H^+]}{K_3} + 1}$$

where: $K_1 = 1.95 \times 10^{-2}$

$K_2 = 7.82 \times 10^{-7}$ (Atlas et al., 1976)

$K_3 = 1.00 \times 10^{-9}$

$(\gamma_{CO_3^{2-}})_T = 0.03$ (Berner, 1971)

$$[CO_3^{2-}]_T = \frac{\text{(titration alkalinity)}}{\frac{[H^+]}{K_2} + 2}$$

where: $K_2 = 7.9 \times 10^{-10}$

$(\gamma_{Mn^{2+}})_T = 3.9 \times 10^{-2}$ (Li et al., 1969)

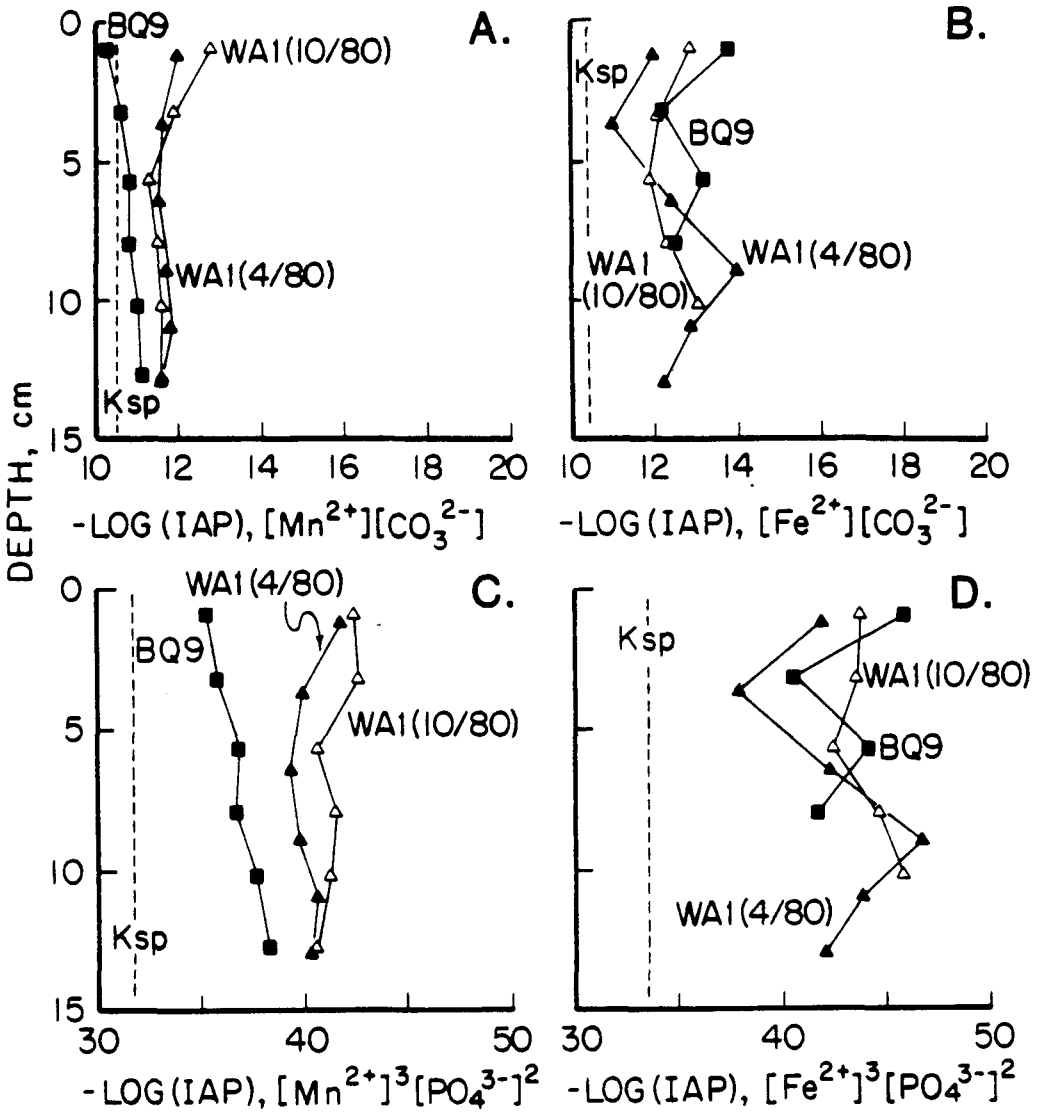


Fig. 12. a. -Log (IAP) vs. depth for rhodochrosite.
b. -Log (IAP) vs. detph for siderite.
c. -Log (IAP) vs. depth for reddingsite.
d. -Log (IAP) vs. depth for vivianite.

mixing and the supply of reactive organic matter control the flux of reactive solutes. Because of frequent mixing in Smeaton Bay, thermodynamic controls on Mn, Fe, and phosphate concentrations are not observed. In contrast, reducing conditions in sediments from the main basin of Boca de Quadra result in large Mn^{2+} fluxes. The interstitial Mn concentrations appear to be in equilibrium with rhodochrosite or similar Mn carbonate.

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Appendix C. Sediment characteristics of interstitial wa

Depth cm	z cm	Mn umol/L	Fe umol/L	Mn ug/g	Cu ug/g
WA2(2) 9/18/80					
0.0- 2.0	1.0	4.7	92.4		
2.0- 4.0	3.0	4.7	29.0		
4.0- 6.0	5.0	5.7	10.7		
6.0- 8.0	7.0	5.4	10.2		
8.0-10.0	9.0	6.2	24.2		
10.0-12.0	11.0	5.4	1.9		
WA2(1) 10/8/80					
0.0- 2.5	1.2	26.8	30.4		
2.5- 4.5	3.5	18.1	202.		
4.5- 7.0	5.8	8.5	193.		
7.0- 9.5	8.2	5.1	104.		
9.5-12.0	10.8	3.8	125.		
12.0-14.0	13.0	5.4	39.6		
WA2(2) 10/9/80					
0.0- 3.5	1.8	5.4	4.3		
3.5- 6.0	4.8	5.2	45.3		
6.0- 8.0	7.0	5.0	91.3		
8.0-10.5	9.2	7.6	143.		
10.5-12.5	11.5	7.4	49.0		
12.5-14.5	13.5	7.6	4.3		
WA2(1) 3/15/81					
0.0- 2.2	1.1		49.1		
2.2- 4.6	3.4		60.7		
4.6- 7.0	5.8		12.7		
7.0- 9.5	8.2		9.0		
9.5-11.9	10.7		5.7		
11.9-14.2	13.1		5.0		
WA2(2) 4/11/81					
0.0- 2.3	1.2	21.7	129.		
2.3- 4.8	3.6	16.0	192.		
4.8- 7.0	5.9	27.0	194.		
7.0- 9.3	6.2	31.2	149.		
9.3-11.6	10.4	24.1	59.3		
11.6-13.8	12.7	14.4	13.1		

ter cores from Smeaton Bay and Boca de Quadra. Trace metals.

Depth cm	z cm	Mn umol/L	Fe umol/L	Mn ug/g	Cu ug/g
WA1(3) 11/19/79					
0.0- 2.4	1.2	24.8	16.4		
2.4- 4.8	3.6	9.5	0.6		
4.8- 7.0	5.9	3.8	1.0		
7.0- 9.4	8.2	8.1	---		
9.4-11.7	10.6	3.6	2.0		
WA1(1) 4/11/80					
0.0- 2.5	1.2		2.7		
2.5- 4.5	3.5		4.3		
4.5- 6.5	5.5		1.9		
6.5- 9.0	7.8		0.4		
9.0-11.0	10.0		0.2		
11.0-13.0	12.0		0.0		
WA1(3) 4/11/80					
0.0- 2.0	1.0	11.2	0.3		
2.0- 4.5	3.2	11.7	2.6		
4.5- 7.0	5.8	13.4	0.8		
7.0- 9.0	8.0	12.9	0.1		
9.0-11.0	10.2	12.0	0.2		
11.5-13.5	12.5	8.8	0.4		
WA1(4) 4/11/80					
0.0- 2.0	1.0	2.7			
2.0- 4.5	3.2	6.2			
4.5- 7.0	5.8	6.0			
7.0- 9.0	8.0	3.4			
9.0-11.5	10.2	5.2			
11.5-14.0	12.8	4.5			
WA1(2) 6/19/80					
0.0- 2.0	1.0	38.6	26.2		
2.0- 4.5	3.2	14.0	16.1		
4.5- 7.0	5.8	5.8	0.1		
7.0- 9.0	8.0	9.5	0.3		
9.0-11.0	10.0	4.5	0.6		
11.0-13.0	12.0	3.9	0.6		

WA2(2) 1/11/82			
0.0- 3.0	1.5	8.1	7.3
3.0- 6.0	4.5	4.6	32.2
6.0- 8.2	7.1	3.1	17.0
8.2-10.5	9.4	9.2	39.7
10.5-13.0	11.8	14.3	85.4
13.0-15.3	14.2	18.7	76.6
WA2(1) 6/6/82			
0.0- 2.5	1.2	2.4	51.2
2.5- 5.4	4.0	2.3	88.8
5.4- 7.8	6.6	1.9	27.9
7.8-10.1	9.0	4.2	12.2
10.1-12.2	11.2	7.8	23.6
12.2-14.7	13.4	10.4	28.5
WA2(1) 8/26/82			
0.0- 2.3	1.2	7.3	34.6
2.3- 4.7	3.5	3.2	46.8
4.7- 7.0	5.8	3.0	17.9
7.0- 9.3	8.2	3.3	2.2
9.3-11.7	10.5	3.5	1.3
11.7-13.8	12.8	2.8	1.1
13.8-15.7	14.8	2.3	1.2
15.7-17.7	16.7	2.5	1.1
17.7-20.1	18.9	2.2	3.2
20.1-22.5	21.3	1.6	0.9
22.5-24.6	23.6	1.1	0.9
24.6-26.7	25.6	0.3	1.2
WA2(2) 8/27/82			
0.0- 2.0	1.0	11.2	14.0
2.0- 4.5	3.2	5.7	65.7
4.5- 6.8	5.6	5.8	38.3
6.8- 9.2	8.0	7.5	22.9
9.2-11.6	10.4	10.2	25.1
11.6-14.0	12.8	8.7	2.9
14.0-16.2	15.1	7.7	1.6
16.2-18.6	17.4	5.9	1.5
18.6-21.0	19.8	3.4	0.6
21.0-23.5	22.2	1.3	0.7
23.5-25.5	24.5	0.3	0.9
25.5-27.5	26.5	0.4	1.7

WA1(3) 9/18/80					
0.0- 2.0	1.0	8.0	0.1		
2.0- 4.5	3.2	10.7	10.6		
4.5- 7.0	5.8	11.7	22.6		
7.0- 9.0	8.0	7.4	15.9		
9.0-11.5	10.2	7.4	1.4		
11.5-13.5	12.5	6.6	5.2		
WA1(2) 10/9/80					
0.0- 2.5	1.2	13.2	16.1		
2.5- 5.0	3.8	26.0	165.		
5.0- 8.0	6.5	22.9	3.5		
8.0-10.0	9.0	15.9	0.1		
10.0-12.0	11.0	9.0	1.0		
12.0-14.0	13.0	7.1	2.5		
WA1(1) 3/14/81					
0.0- 2.5	1.2		14.9	552	46
2.5- 5.2	3.8		72.8	487	43
5.2- 7.7	6.4		99.4	500	39
7.7-10.2	9.0		157.	500	46
10.2-13.0	11.6		137.	524	42
13.0-16.0	14.5		77.2	498	48
WA1(1) 4/11/81					
0.0- 2.6	1.3	3.5	0.2		
2.6- 5.1	3.8	4.4	15.7		
5.1- 7.0	6.0	3.7	1.1		
7.0- 9.0	8.0	2.8	1.1		
9.0-10.9	10.0	3.6	4.0		
10.9-13.1	12.0	3.0	4.6		
WA1(2) 4/12/81					
0.0- 2.7	1.4	8.4	5.9		
2.7- 5.0	3.8	9.8	14.3		
5.0- 7.3	6.2	6.3	5.9		
7.3- 9.5	8.4	5.9	1.7		
9.5-11.9	10.7	5.5	0.8		
11.9-14.2	13.0	5.2	0.9		
WA1(3) 8/10/81					
0.0- 2.3	1.2	8.2	0.1		
2.3- 4.8	3.6	11.8	29.9		
4.8- 7.1	6.0	11.5	17.0		
7.1- 9.8	8.4	13.0	43.7		

Depth cm	z cm	Mn umol/L	Fe umol/L	Mn ug/g	Cu ug/g
WA1(3) 8/10/81 (cont.)					
9.8-12.0	10.9	13.5	26.5		
12.0-14.3	13.2	10.0	0.7		
WA1(1) 8/26/82					
0.0- 2.0	1.0	9.9	0.2		
2.0- 4.3	3.2	8.8	5.6		
4.3- 6.8	5.6	7.2	2.3		
6.8- 9.0	7.9	6.0	0.2		
9.0-11.4	10.2	5.0	0.2		
11.4-13.7	12.6	4.9	0.2		
13.7-16.2	15.0	4.7	0.2		
16.2-18.2	17.2	4.2	0.2		
18.2-20.5	19.4	4.2	0.2		
20.5-22.8	21.6	3.8	0.3		
22.8-25.2	24.0	3.5	1.2		
25.2-27.7	26.4	2.8	0.2		
WA1(2) 8/28/82					
0.0- 2.0	1.0	15.1	1.7	392	61
2.0- 4.5	3.2	8.5	5.8	392	58
4.5- 6.8	5.6	9.2	0.6	376	60
6.8- 9.2	8.0	6.4	0.8	380	59
9.2-11.4	10.3	5.1	0.5	388	59
11.4-13.7	12.6	4.6	0.6	375	54
13.7-16.0	14.8	4.7	0.4	388	55
16.0-18.2	17.1	5.2	0.3	392	49
18.2-20.5	19.4	4.0	0.3	396	54
20.5-23.0	21.8	3.1	0.9	381	50
23.0-25.4	24.2	2.5	0.5	392	49
25.4-27.8	26.6	2.3	1.1	380	49
SB0(1) 3/14/81					
0.0- 2.0	1.0	16.8	5.0		
2.0- 4.5	3.2	9.3	89.0		
4.6- 6.6	5.6	10.2	49.6		
6.6- 9.0	7.8	11.0	61.1		
9.0-11.2	10.1	11.2	47.4		
11.2-13.7	12.4	10.0	27.9		

Depth cm	z cm	Mn umol/L	Fe umol/L	Mn ug/g	Cu ug/g
SB1(1) 6/13/81					
0.0- 1.5	0.8	24.3	2.2	338	70
1.5- 3.9	2.7	11.5	53.0	340	65
3.9- 6.2	5.0	9.9	55.3	352	60
6.2- 8.6	7.4	8.2	22.3	336	82
8.6-10.9	9.8	7.4	8.6	305	74
10.9-13.3	12.1	7.2	12.2	340	100
SB1(1) 8/9/81					
0.0- 2.0	1.0	11.6	0.3		
2.0- 4.5	3.2	9.4	11.3		
4.5- 7.0	5.8	7.3	2.5		
7.0- 9.4	8.2	7.1	2.1		
9.4-12.0	10.7	7.4	0.6		
12.0-14.3	13.2	7.1	1.6		
SB1(1) 9/15/81					
0.0- 1.7	0.8	17.2	15.7		
1.7- 4.1	2.9	5.2	2.2		
4.1- 6.6	5.4	4.1	1.7		
6.6- 8.8	7.7	4.4	0.8		
8.8-11.4	10.1	5.0	1.1		
11.4-13.7	12.6	5.1	2.4		
SB1(1) 1/12/82					
0.0- 2.0	1.0	4.6	--		
2.0- 4.0	3.0	3.7	18.1		
4.0- 5.8	4.9	11.5	6.2		
5.8- 8.3	7.0	6.3	41.2		
8.3-10.7	9.5	4.8	22.2		
10.7-13.3	12.0	4.5	9.7		
SB1(1) 4/11/82					
0.0- 2.0	1.0	17.3	12.0		
2.0- 4.5	3.2	19.3	97.9		
4.5- 6.8	5.6	15.8	33.3		
6.8- 9.4	8.1	11.9	41.5		
9.4-11.8	10.6	12.7	45.1		
11.8-13.8	12.8	12.7	29.5		

SBO(1) 6/15/81					
0.0- 2.4	1.2	23.9	10.2		
2.4- 4.8	3.6	14.7	35.6		
4.8- 7.0	5.9	7.9	15.2		
7.0- 9.4	8.2	6.4	10.8		
9.4-11.9	10.6	5.5	7.1		
11.9-14.2	13.0	5.2	2.0		
SBO(1) 4/13/82					
0.0- 2.4	1.2	24.8	34.7		
2.4- 4.8	3.6	18.0	114.		
4.8- 7.0	5.9	11.7	96.2		
7.0- 9.3	8.2	10.4	149.		
9.3-11.8	10.6	9.7	137.		
11.8-14.0	12.9	9.0	96.3		
SBO(1) 8/26/82					
0.0- 2.0	1.0	28.6	98.1		
2.0- 4.5	3.2	14.7	79.9		
4.5- 6.7	5.6	7.6	4.4		
6.7- 9.2	8.0	5.4	11.0		
9.2-11.7	10.4	8.0	10.7		
11.7-14.1	12.9	5.7	15.0		
14.1-16.7	15.4	6.5	8.3		
16.7-19.2	18.0	6.4	8.6		
19.2-21.9	20.6	6.4	10.9		
21.9-24.2	23.0	6.6	6.7		
48.0-50.0	49.0	4.4	1.7		
50.0-52.3	51.2	3.9	1.1		
SB1(2) 3/14/81					
0.0- 2.8	1.4		40.8	441	48
2.8- 5.2	4.0		32.6	433	46
5.2- 7.5	6.4		12.0	436	46
7.5-10.0	8.8		15.0	441	46
10.0-12.5	11.2		5.6	446	44
12.5-15.0	13.8		11.0	440	47
SB1(1) 3/13/81					
0.0- 2.5	1.2	7.1	2.4		
2.5- 4.7	3.6	11.8	174.		
4.7- 7.4	6.0	7.4	26.1		
7.4- 9.1	8.2	8.1	36.2		
9.8-12.2	11.0	6.8	13.9		
12.2-14.8	13.5	6.2	7.9		

SB1(1) 8/25/82					
0.0- 2.1	1.0	23.9	8.2	319	116
2.1- 4.6	3.4	5.7	12.2	340	76
4.6- 7.1	5.8	3.9	1.7	358	68
7.1- 9.8	8.4	3.4	3.0	339	58
9.8-12.0	10.9	3.9	1.2	382	72
12.0-14.3	13.2	4.4	0.0	350	114
14.3-16.7	15.5	4.6	1.2	338	68
16.7-19.3	18.0	4.8	1.6	345	73
19.3-21.6	20.4	4.7	0.7	342	51
21.6-24.0	22.8	4.8	0.9	375	68
24.0-26.5	24.8	5.0	0.4	358	71
26.5-28.8	27.6	4.7	0.3	345	71
BQ9(3) 6/17/80					
0.0- 2.5	1.2		1.0		
2.5- 5.0	3.8		2.7		
5.0- 7.0	6.0		0.8		
7.0- 9.5	8.2		0.6		
9.5-11.5	10.5		0.7		
11.5-13.5	12.5		0.6		
BQ9(4) 6/17/80					
0.0- 3.0	1.5		1.4		
3.0- 5.0	4.0		7.4		
5.0- 7.5	6.2		0.8		
7.5-10.0	8.8		0.4		
10.0-12.0	11.0		0.1		
12.0-14.5	13.2		0.4		
BQ9(1) 8/11/80					
0.0- 2.0	1.0		0.6		
2.0- 4.5	3.2		19.3		
4.5- 7.0	5.8		5.9		
7.0- 9.5	8.2		1.5		
9.5-11.5	10.5		0.6		
11.5-14.0	12.8		1.2		
BQ9(1) 9/19/80					
0.0- 2.0	1.0		0.3		
2.0- 4.5	3.2		16.8		
4.5- 7.0	5.8		0.8		
7.0- 9.0	8.0		0.6		
9.0-11.0	10.0		0.1		
11.0-13.0	12.0		1.7		

Depth cm	z cm	Mn umol/L	Fe umol/L	Mn ug/g	Cu ug/g
BQ9(4) 9/24/80					
0.0- 3.0	1.5		0.2		
3.0- 5.5	4.2		33.0		
5.5- 8.0	6.8		1.5		
8.0-10.5	9.2		1.6		
10.5-13.0	11.8		0.4		
13.0-15.0	14.0		0.1		
BQ9(5) 9/24/80					
0.0- 2.5	1.2		--		
2.5- 5.0	3.8		44.7		
5.0- 7.5	6.2		3.9		
7.5-10.0	8.8		1.4		
10.0-12.0	11.0		2.4		
12.0-14.5	13.2		1.4		
BQ9(2) 10/13/80					
0.0- 2.0	1.0	504.	0.2		
2.0- 4.5	3.2	159.	6.1		
4.5- 7.0	5.8	101.	0.5		
7.0- 9.0	8.0	82.6	2.5		
9.0-11.5	10.2	46.4	0.2		
11.5-14.0	12.8	35.7	0.2		
BQ9(1) 4/13/81					
0.0- 2.1	1.0		1.2		
2.1- 4.7	3.4		4.4		
4.7- 7.1	5.9		5.2		
7.1- 9.5	8.3		2.0		
9.5-12.0	10.8		1.2		
12.0-14.5	13.2		1.1		
BQ9(2) 4/14/81					
0.0- 2.3	1.2		0.8	1491	71
2.3- 4.6	3.4		9.6	957	36
4.6- 7.0	5.8		2.9	870	40
7.0- 9.2	8.1		4.0	842	38
9.2-11.2	10.2		0.7	874	39
11.2-12.7	12.0		1.2	834	38

BQ9(2) 8/2/81

0.0- 2.6	1.3		0.1
2.6- 4.9	3.8		0.6
4.9- 7.5	6.2		2.0
7.5-10.0	8.8		0.7
10.0-12.5	11.2		0.1
12.5-15.0	13.8		0.2

BQ9(1) 9/1/82

0.0- 1.5	0.8	268	1.0	889	63
1.5- 3.8	2.6	167	2.5	747	96
3.8- 6.2	5.0	62.8	0.6	622	56
6.2- 8.7	7.4	43.9	0.2	628	55
8.7-10.7	9.7	40.3	0.8	666	48
10.7-13.0	11.8	32.6	0.3	702	46
13.0-15.4	14.2	31.1	0.2	679	48
15.4-17.7	16.6	23.8	0.2	697	50
17.7-20.0	18.8	24.5	0.2	742	51
20.0-22.2	21.1	27.8	0.2	711	49
22.2-25.0	23.6	25.5	0.2	650	46
25.0-27.5	26.2	24.0	0.2	619	43

Appendix D. Sediment characteristics of interstitial wat

Depth cm	z cm	PO_4 umol/L	NO_3 umol/L	NO_2 umol/L	NH_4 umol/L
WA2(1) 6/20/80					
0.0- 1.5	0.8	11.84	1.12	0.32	20.32
1.5- 4.0	2.8	10.08	1.28	0.16	36.48
4.0- 6.0	5.0	19.68	1.60	0.16	83.36
6.0- 8.0	7.0	30.72	1.60	0.16	126.6
8.0- 9.5	8.8	72.16	1.44	0.32	148.2
9.5-12.0	10.8	33.92	1.60	0.16	156.5
WA2(1) 8/7/80					
0.0- 2.0	1.0	---	0.96	0.32	9.92
2.0- 4.5	3.2	11.42	0.96	0.32	36.16
4.5- 7.0	5.8	8.16	0.80	0.32	49.60
7.0- 9.0	8.0	26.40	0.80	0.32	61.60
9.0-11.0	10.0	8.80	0.80	0.16	76.16
11.0-13.0	12.0	14.88	0.64	0.16	91.84
WA2(1) 10/8/80*					
0.0- 2.5	1.2	1.92	0.0	5.12	38.15
2.5- 4.5	3.5	19.39	0.0	18.75	74.15
4.5- 7.0	5.8	25.15	0.0	15.87	67.33
7.0- 9.5	8.2	3.86	0.0	8.50	75.12
9.5-12.0	10.8	83.34	0.0	9.62	208.4
12.0-14.0	13.0	112.2	0.0	5.38	283.1
WA2(1) 12/13/80					
0.0- 2.5	1.2	8.91	0.0	0.66	11.22
2.5- 5.0	3.8	10.78	0.0	1.54	19.36
5.0- 7.5	6.2	28.05	0.0	0.77	35.75
7.5-10.0	8.8	42.68	0.0	0.66	57.53
10.0-12.5	11.2	66.99	0.0	0.55	70.51
12.5-15.0	13.8	85.60	0.0	0.64	81.76
WA2(2) 12/14/80					
0.0- 2.0	1.0	5.60	0.0	0.32	5.28
2.0- 4.0	3.0	17.05	0.0	0.22	19.58
4.0- 7.0	5.5	37.40	0.0	0.33	69.30
7.0- 9.0	8.0	57.53	0.0	0.33	114.0
9.0-11.5	10.2	92.95	0.0	0.44	176.1
11.5-14.0	12.8	153.1	0.0	0.66	226.0

ter cores from Smeaton Bay and Boca de Quadra. Nutrients.

Depth cm	z cm	PO_4 umol/L	NO_3 umol/L	NO_2 umol/L	NH_4 umol/L
WA1(3) 4/11/80*					
0.0- 2.0	1.0	1.42	0.0	2.21	17.79
2.0- 4.5	3.2	9.43	0.0	1.18	68.74
4.5- 7.0	5.8	13.03	0.0	0.54	96.64
7.0- 9.0	8.0	17.08	0.0	0.76	104.6
9.0-11.5	10.2	40.59	0.0	1.12	113.0
11.5-13.5	12.5	30.06	0.0	1.22	111.2
WA1(1) 6/19/80					
0.0- 2.0	1.0	2.56	1.28	0.48	2.72
2.0- 4.0	3.0	5.28	0.0	0.0	24.32
4.0- 5.5	4.8	8.32	0.64	0.16	43.68
5.5- 8.0	6.8	17.92	0.96	0.16	60.16
8.0-10.0	9.0	17.92	0.80	0.32	70.24
10.0-11.5	10.8	16.64	0.96	0.48	79.20
WA1(3) 9/18/80*					
0.0- 2.0	1.0	2.78	0.0	3.62	7.16
2.0- 4.5	3.2	2.92	0.0	2.62	21.15
4.5- 7.0	5.8	4.73	0.0	7.00	26.53
7.0- 9.0	8.0	2.23	0.0	2.88	33.12
9.0-11.5	10.2	2.27	0.0	3.25	43.49
11.5-13.5	12.5	8.34	0.0	3.25	52.66
WA1(1) 10/8/80					
0.0- 2.5	1.2	3.64	0.0	0.32	5.60
2.5- 5.0	3.8	10.85	0.0	0.0	16.48
5.0- 7.0	6.0	17.08	0.0	0.16	31.68
7.0- 9.5	8.2	21.35	0.0	0.48	47.84
9.5-12.0	10.8	17.08	0.0	2.48	52.70
12.0-14.0	13.0	17.70	0.0	2.17	58.28
WA1(1) 3/14/81					
0.0- 2.5	1.2	1.92	0.0	0.80	2.56
2.5- 5.2	3.8	23.36	0.0	0.96	5.28
5.2- 7.7	6.4	56.00	0.0	0.96	12.16
7.7-10.2	9.0	38.28	0.0	1.60	21.28
10.2-13.0	11.6	125.0	0.0	2.40	23.36
13.0-16.0	14.5	41.92	0.0	0.96	26.56

WA2(1) 4/11/81					
0.0- 2.8	1.4	3.74	12.46	0.44	19.25
2.8- 5.3	4.0	61.60	1.43	0.77	90.53
5.3- 7.7	6.5	104.6	0.0	0.77	176.6
7.7-10.1	8.9	144.0	1.60	1.60	220.5
10.1-12.5	11.3	89.12	0.0	0.80	25.14
12.5-15.0	13.8	74.24	0.0	0.80	280.8
WA2(1) 1/11/82					
0.0- 3.5	1.8	1.28	0.0	0.16	22.24
3.5- 6.5	5.0	10.24	0.0	0.48	48.96
6.5- 9.0	7.8	10.72	0.0	0.16	48.48
9.0-11.5	10.3	12.80	0.0	0.01	50.72
11.5-14.0	12.8	17.76	0.0	0.0	61.92
14.0-16.5	25.2	16.48	0.0	0.0	74.08
WA1(2) 11/19/79					
0.0- 2.4	1.2	4.06	0.35	0.0	13.96
2.4- 4.9	3.6	34.58	0.78	0.0	79.30
4.9- 7.2	6.0	42.84	0.0	0.0	100.5
7.2- 9.5	8.4	31.62	0.0	0.0	109.2
9.5-12.0	10.8	36.39	0.0	0.0	112.5
12.0-14.0	13.0	39.93	0.0	0.0	109.7
WA1(2) 4/11/80					
0.0- 2.5	1.2	8.80	2.24	0.48	19.20
2.5- 5.0	3.8	2.40	2.88	0.0	56.64
5.0- 6.0	5.5	6.72	9.12	0.0	54.72
6.0- 7.5	6.8	6.22	0.62	0.62	46.50
7.5-10.0	8.8	7.75	0.0	0.0	51.77
10.0-12.5	11.2	16.74	4.34	0.0	57.04

WA1(2) 4/12/81*					
0.0- 2.7	1.4	3.01	0.34	3.50	13.52
2.7- 5.0	3.8	6.65	0.0	1.63	63.63
5.0- 7.3	6.2	9.21	0.0	1.25	116.5
7.3- 9.5	8.4	23.03	0.0	1.25	125.0
9.5-11.9	10.7	13.75	0.0	1.37	129.7
11.9-14.2	13.0	19.36	0.0	1.25	143.1
WA1(1) 8/8/81					
0.0- 2.5	1.2	3.68	0.0	0.80	10.40
2.5- 4.8	3.6	5.60	0.0	0.48	24.48
4.8- 7.3	6.0	5.44	0.0	0.48	42.24
7.3- 9.8	8.6	5.44	0.0	0.48	60.16
9.8-12.1	11.0	7.04	0.0	0.48	67.68
12.1-14.6	13.4	7.20	0.0	0.48	76.32
WA1(2) 8/8/81					
0.0- 2.2	1.1	0.96	0.0	0.32	8.32
2.2- 4.7	3.4	9.44	0.0	0.16	32.00
4.7- 7.1	5.9	9.12	0.0	0.16	47.04
7.1- 9.3	8.2	9.60	0.0	0.16	63.04
9.3-11.8	10.6	10.72	0.0	0.32	72.64
11.8-14.2	13.0	13.76	0.0	0.16	81.76
WA1(3) 8/10/81*					
0.0- 2.3	1.2	3.54	0.08	3.45	10.24
2.3- 4.8	3.6	10.35	0.0	1.02	46.29
4.8- 7.1	6.0	15.94	6.54	27.96	71.50
7.1- 9.8	8.4	15.90	0.0	5.78	75.55
9.8-12.0	10.9	6.75	0.0	3.60	81.84
12.0-14.3	13.2	7.93	0.0	2.17	77.12

Depth cm	z cm	PO_4 umol/L	NO_3 umol/L	NO_2 umol/L	NH_4 umol/L
SBO(1) 6/19/80					
0.0- 2.0	1.0	8.98	0.0	0.16	10.72
2.0- 4.5	3.2	13.44	0.0	0.32	36.80
4.5- 7.0	5.8	13.44	0.0	0.16	36.80
7.0- 9.5	8.2	8.16	0.0	0.16	28.32
9.5-12.0	10.8	8.80	0.0	0.16	32.00
12.0-14.0	13.0	12.64	0.0	0.32	48.00
SBO(1) 12/14/80					
0.0- 2.5	1.2	4.51	0.0	0.10	4.40
2.5- 5.0	3.8	16.06	0.0	0.10	22.99
5.0- 7.5	6.2	18.70	0.0	0.10	37.62
7.5-10.0	8.8	17.38	0.0	0.20	47.30
10.0-12.5	11.2	19.25	0.0	0.20	53.57
12.5-15.0	13.8	26.40	0.0	0.10	74.03
SBO(1) 8/26/82					
0.0- 2.0	1.0	22.40	0.0	0.16	16.48
2.0- 4.5	3.2	18.80	0.0	0.16	47.04
4.5- 6.7	5.6	9.12	0.0	0.16	59.68
6.7- 9.2	8.0	20.16	0.0	0.48	64.16
9.2-11.7	10.4	15.20	0.0	0.16	67.84
11.7-14.1	12.9	22.40	0.0	0.16	76.96
14.1-16.7	15.4	24.96	0.0	0.16	92.32
16.7-19.2	18.0	28.48	0.0	0.16	104.3
19.2-21.9	20.6	25.44	0.16	0.16	116.3
21.9-24.2	23.0	38.24	0.16	0.16	130.7
48.0-50.0	49.0	34.56	0.0	0.16	135.0
50.0-52.3	51.2	24.48	0.0	0.16	90.88
SB1(2) 12/13/80					
0.0- 3.0	1.5	1.76	0.0	0.33	5.94
3.0- 5.5	4.2	7.15	0.0	0.11	21.34
5.5- 8.0	6.8	8.69	0.0	0.0	17.60
8.0-10.5	9.2	10.56	0.0	0.22	32.67
10.5-13.0	11.8	9.56	0.0	0.0	24.20
13.0-16.0	14.5	12.65	0.0	0.0	28.60

Depth cm	z cm	PO_4 umol/L	NO_3 umol/L	NO_2 umol/L	NH_4 umol/L
BQ9(1) 6/17/80					
0.0- 2.0	1.0	48.32	0.0	0.32	37.76
2.0- 4.5	3.2	25.60	0.0	0.16	73.60
4.5- 7.0	5.8	34.56	0.0	0.16	99.68
7.0- 9.0	8.0	29.44	0.0	0.16	107.2
9.0-11.5	10.2	28.00	0.0	0.32	124.8
11.5-14.0	12.8	23.68	0.0	0.32	126.4
BQ9(1) 9/19/80*					
0.0- 2.0	1.0	52.56	0.0	2.20	77.68
2.0- 4.5	3.2	68.64	0.0	0.65	187.9
4.5- 7.0	5.8	62.98	0.0	0.34	212.3
7.0- 9.0	8.0	61.43	0.0	0.0	223.7
9.0-11.0	10.0	39.97	0.0	0.0	235.1
11.0-13.0	12.0	52.25	0.02	0.05	241.7
BQ9(2) 9/19/80					
0.0- 2.0	1.0	33.22	1.65	0.55	38.17
2.0- 4.5	3.2	72.38	0.55	0.33	133.5
4.5- 7.0	5.8	55.66	0.11	0.33	161.0
7.0- 9.5	8.2	40.26	0.11	0.33	182.0
9.5-11.5	10.5	32.56	0.0	0.33	193.7
11.5-14.0	12.8	29.04	0.0	0.33	185.4
BQ9(3) 9/23/80					
0.0- 3.5	1.8	21.60	8.64	1.76	47.20
3.5- 6.0	4.8	104.5	5.60	1.28	85.60
6.0- 8.5	7.2	58,24	5.60	1.44	143.2
8.5-11.0	9.8	49.92	4.80	2.24	159.8
11.0-13.0	12.0	47.52	4.32	1.92	171.5
13.0-16.0	14.5	41.92	5.44	0.96	178.2
BQ9(1) 10/12/80					
0.0- 2.5	1.2	29.76	0.0	0.96	18.72
2.5- 5.0	3.8	72.16	0.0	0.48	73.12
5.0- 8.0	6.5	41.76	0.0	0.48	98.88
8.0-10.0	9.0	50.56	0.0	0.48	132.8
10.0-12.5	11.2	41.28	0.0	0.80	150.4
12.5-15.0	13.8	29.60	0.0	0.32	152.0

SB1(1) 3/13/81					
0.0- 2.5	1.2	1.87	0.55	0.66	5.28
2.5- 4.7	3.6	8.64	0.32	0.80	9.92
4.7- 7.4	6.0	14.08	0.0	0.64	13.44
7.4- 9.1	8.2	20.00	0.0	0.64	17.44
9.1-12.2	11.0	18.72	0.0	0.48	15.22
12.2-14.8	13.5	17.12	0.0	0.48	17.28
SB1(1) 4/11/81					
0.0- 3.8	1.9	4.62	0.77	0.22	12.21
3.8- 6.2	5.0	24.53	0.33	0.33	57.64
6.2- 8.7	7.4	20.68	0.66	0.44	81.07
8.7-11.1	9.9	20.32	0.0	0.32	84.80
11.1-13.5	12.3	10.56	0.0	0.32	90.08
13.5-16.0	14.8	9.76	0.0	0.32	91.36
SB1(1) 8/9/81*					
0.0- 2.0	1.0	4.58	0.0	2.30	27.51
2.0- 4.5	3.2	18.21	0.0	1.03	87.57
4.5- 7.0	5.8	18.16	0.0	0.38	88.81
7.0- 9.4	8.2	17.20	0.0	0.73	91.26
9.4-12.0	10.7	19.73	0.0	0.58	91.47
12.0-14.3	13.2	19.84	0.0	0.94	93.91
SB1(2) 8/9/81					
0.0- 2.6	1.3	10.24	3.36	0.32	6.24
2.6- 4.8	3.7	19.52	1.12	0.32	27.84
4.8- 7.2	6.0	18.88	0.16	0.16	36.00
7.2- 9.4	8.3	6.40	0.0	0.16	35.68
9.4-11.7	10.6	3.52	0.0	0.16	33.28
11.7-14.0	12.8	6.72	0.0	0.16	29.92
SB1(1) 4/11/82*					
0.0- 2.0	1.0	7.35	0.0	2.09	17.49
2.0- 4.5	3.2	22.21	0.0	6.53	41.32
4.5- 6.8	5.6	7.59	0.0	2.10	42.97
6.8- 9.4	8.1	15.91	0.0	2.42	60.61
9.4-11.8	10.6	20.59	0.0	2.12	69.48
11.8-13.8	12.8	12.96	0.0	2.06	67.34

BQ9(3) 4/15/81					
0.0- 2.5	1.2	8.25	0.99	0.33	17.60
2.5- 4.8	3.6	51.37	0.22	0.33	73.81
4.8- 7.6	6.2	59.04	0.0	0.48	108.3
7.6-10.2	8.9	47.52	0.16	0.32	130.7
10.2-12.7	11.4	33.12	0.16	0.32	135.8
12.7-15.0	13.8	22.72	0.0	0.32	122.9
BQ9(1) 8/2/81					
0.0- 2.2	1.1	20.00	0.0	0.48	17.60
2.2- 4.8	3.5	24.48	0.0	0.32	23.52
4.8- 7.3	6.0	63.20	0.0	0.32	65.92
7.3- 9.6	8.4	26.72	0.0	0.32	65.76
9.6-12.2	10.9	23.68	0.0	0.48	59.84
12.2-14.5	13.4	17.28	0.0	0.48	97.12
BQ9(1) 9/16/81					
0.0- 2.1	1.1	12.32	4.16	0.16	34.08
2.1- 4.5	3.3	46.40	0.96	0.16	80.80
4.5- 6.8	5.6	25.60	1.12	0.16	73.92
6.8- 9.2	8.0	16.16	0.80	0.16	63.20
9.2-11.8	10.5	13.14	0.32	0.16	67.20
11.8-13.8	12.8	15.84	0.32	0.16	83.84

5. Postscript (What Does This Mean?) and Thesis Summary

At the outset of this investigation, my objective was to determine the importance of natural organic matter (both terrestrial and marine) on the diagenesis of trace metals in the sediments of Smeaton Bay and Boca de Quadra. I assumed that because the bottom waters of these silled fjords were virtually isothermal and advectively isolated for most of the year, sediment processes would be steady state. However, as demonstrated in the previous chapters, the factors controlling trace metal and nutrient geochemistry in my study area are complex and varied. In fact, the most obvious conclusion of this thesis is that average fluxes of metals, nutrients, carbon, and bulk sediment do not exist, except in a conceptual sense for very limited areas of the fjords. Because a large percentage of the yearly export from the rivers can occur in a single storm event, and because the sedimentation within these steep-sided fjords is punctuated by episodic slumping and post-depositional mixing, conditions observed on a given sampling date cannot easily be extrapolated to predict conditions on a yearly or longer interval. While these are not conditions unique to Smeaton Bay and Boca de Quadra, I believe that the close interaction between terrestrial and marine environments arising from the high relief and extreme precipitation makes spatial and temporal variability more important in these fjords than elsewhere. Perhaps one of the greatest misconceptions to which a graduate student can succumb is that "one more sample" will untangle the complexities of a natural system. Two hundred and three cores and

countless water samples later, I find that I'm no closer to setting boundaries on a "well-behaved" system than I was at the outset. From a geochemical standpoint, Smeaton Bay and Boca de Quadra may be two of the better studied fjords (certainly in Alaska), but the quantification of biogeochemical cycles remains poorly understood. Detailed mass balances of nutrients and carbon have been derived using some of the data in this thesis (Burrell, 1984) and work in progress (Hong, in prep.), employing sediment traps to collect material for determinations of carbon isotopes, as well as major and minor elements, will better quantify sediment inputs. However, in this final chapter, I present some rough calculations of Mn fluxes which may be compared with studies from other coastal areas. The reader is cautioned that in addition to the variability observed in the interstitial water profiles from which the diffusion-predicted fluxes are calculated, the bottom topography of Smeaton Bay and Boca de Quadra is not well mapped. As better estimates for the surface area of active sedimentation become available, flux measurements will be refined.

COMPARISON OF MANGANESE FLUXES IN COASTAL ENVIRONMENTS

Decomposition of organic matter is highly temperature dependent (e.g. Aller and Yingst, 1980), and thus I expected that fluxes of reactive solutes from the sediments of Smeaton Bay and Boca de Quadra would be lower than similar measurements made in temperate estuaries. However, the calculated Mn flux from sediments at the deep basin station in Boca de Quadra is greater than most reported fluxes (Table

1) based upon calculations from pore water profiles (DP, diffusion predicted) and direct measurements (DM). Higher Mn fluxes were observed in shallow waters of the Mexico continental shelf (Sawlan and Murray, 1983) and in Long Island Sound (Aller, 1980), but water temperatures there were much higher than in Boca de Quadra. The sediments from the main basin of Smeaton Bay are less reducing than those from the main basin of Boca de Quadra (Chapter 3,4), resulting in substantially lower Mn fluxes.

MASS BALANCE CONSIDERATIONS FOR MANGANESE IN SMEATON BAY AND BOCA DE QUADRA

During estuarine mixing, the behavior of Mn is generally regarded as non-conservative (Sholkovitz, 1978), with solublization of Mn from suspended particulates (Wilke and Dayal, 1982) and reducing sediments (Evans et al., 1977, Sundby et al., 1981, Trefry and Presley, 1982) contributing dissolved Mn to the water column. Recognizing that in a fjord such as Smeaton Bay, the river input of Mn in the surface waters is effectively decoupled from the deep waters receiving the diffusive sediment flux of Mn, an estimate of the relative importance of the two inputs was made. Because water column profiles of Mn were not measured, actual mass balances are impossible. Using the annual export of total Mn from the Wilson and Blossom Rivers (Chapter 2), the riverine contribution of Mn to Seaton Bay is 124 kmol yr^{-1}. The surface area of Smeaton Bay including Wilson and Bakewell Arms is 33 km^2, which I have divided into Wilson Arm (excluding the Wilson-Blossom tide-flats): 9.3 km^2; Bakewell Arm: 4.2 km^2; and Smeaton Bay

Table 1. Benthic Manganese Fluxes

Sta.	Location	Lat. N°	Type	Temp. °C	Water depth m	Flux μmol $cm^{-2}yr^{-1}$	Ref.
BQ9	Boca de Quadra	55	DP	6	368	38.7	1
BQ3					156	1.6	
BQ3A					145	0.4	
SB0	Smeaton Bay				241	3.1	
SB1					252	2.4	
SB3					259	1.9	
MA1A	Marten Arm				208	5.7	
MA1					174	0.4	
WA2	Wilson Arm				127	0.9	
WA1					152	1.6	
WA0					162	1.2	
BA1	Bakewell Arm				156	1.3	
8	Mississippi Delta	29	DP	21	30	15.3	2
7						11.6	
10					50	9.3	
31					50	15.1	
12					60	10.0	
16					110	6.0	
14					150	0.5	
	Kiel Bight	54	DM	13	27	13.2(aerobic) 41.1(anoxic)	3
FOAM	Long Island Sound	41	DM	22	8	24.4	4
				15		5.8	
				4		2.9	
			DP	22		62.0	
				15		22.6	
				4		9.1	
NWC			DM	22	15	135.0	
				15		127.8	
				4		1.1	
			DP	22		58.4	
				15		32.8	
				4		3.6	
DEEP			DM	22	34	51.1	
				15		3.5	
				4		0.5	
			DP	22	34	29.2	
				15		20.4	
				4		3.3	
	Narragansett Bay	40	DP DM			7.3 (17.8)	5
	Washington slope	47	DP		672	0.02	6
10	Mexico continental shelf	25	DP	10	251	25	7
14		21			42	314	
15					338	44	
16					332	11	
RES2.5	Resurrection Bay	60	DP	5	290	12.6	8

References:
1- This study
2- Trefry and Presley (1982)
3- Balzer (1982)
4- Aller (1980)
5- McCaffrey *et al.* (1980)
6- Jones and Murray (1985)
7- Sawlan and Murray (1983)
8- Heggie and Burrell (1980)

basin: 17.2 km². Assuming that sediment accumulates only on moderately sloped areas, I determined that the area of Smeaton Bay deeper than 200 m amounted to 7.2 km² or 42% of the surface area. Applying this same factor to Wilson and Bakewell Arms, I obtained 3.9 and 1.8 km², respectively, for the areas of active sedimentation. In Boca de Quadra, where more detailed bathymetry is available, G. Hong (Institute of Marine Science, Univ. of Alaska, personal communication) has determined areas of active sedimentation for the innermost basin: 5.5 km² or 47% of the surface area; and 4.5 km² or 28% of the surface area for the deepest basin. The diffusion-predicted Mn fluxes were calculated using interstitial water profiles obtained in August-September 1982 (Chapter 3). A mean of the fluxes obtained for stations within a basin was used to calculate the annual Mn contribution from each region. The amount of Mn "permanently" buried in the sediment was estimated from the product of the mass sediment accumulation and the solid phase Mn concentration below the surface mixed layer. The results of these calculations are shown in Table 2. For Smeaton Bay, 44% of the river input is buried. The total sediment flux of Mn from Smeaton Bay (including Wilson and Bakewell Arms) is 249 kmol yr^{-1}, or twice that supplied by the Wilson-Blossom Rivers. This suggests that there is "excess" Mn remobilized from the fjord sediments over that delivered by the river.

This apparent "excess" Mn may result from an underestimation of the fresh water flux. As seen in Chapter 2, large concentrations of soluble Mn and Fe are supplied to the rivers from the muskegs when the

Table 2. Mass Balance Calculations for Manganese

(All fluxes in units of kmol yr^{-1})

SMEATON BAY

Inputs

Wilson-Blossom River	124	
Secondary streams	40	Estimate
Sediment fluxes:		
Smeaton Bay	178	
Wilson Arm	48	
Bakewell Arm	23	
Atmospheric	Unknown	
Recycling within water column	Unknown	
Sources outside fjord	Unknown	
TOTAL MEASURED INPUTS	249	

Outputs

Burial:		
Smeaton Bay	31	
Wilson Arm	15	
Bakewell Arm	9	
Transport out of fjord	Unknown	
TOTAL MEASURED OUTPUTS	45	

BOCA DE QUADRA

Sediment fluxes:	
Boca de Quadra (second basin)	1740
Boca de Quadra (inner basin)	55
Permanently buried:	
Boca de Quadra (second basin)	50

watershed is flushed following an extended dry period. Also, secondary streams that enter the fjord throughout its length contribute unmeasured Mn. To evaluate the contribution of smaller streams, I calculated the Mn flux for Falsegate Creek (Fig. 1) using the mean from 8 stream flow measurements and 5 Mn determinations (Appendix E). The mean annual flow of 2.4 $m^3 s^{-1}$ and Mn concentration of 83.8 umol m^{-3} result in an annual flux of 2.6 kmol yr^{-1}, or less than 2% of the estimated river input. Because the Wilson-Blossom River drains only 57% of the watershed of Smeaton Bay while smaller streams around the perimeter of the fjord drain the remaining 43%, a significant underestimation in the freshwater flux of Mn is likely. Manganese determinations in several minor streams (Bakewell Arm Creek, Tunnel Creek, Creek draining Lake 793, Fig. 1) indicate that concentrations of Mn and Fe are frequently higher in these creeks than in the Wilson-Blossom River (Fig. 2). However, because of the much smaller volume of water transported by the secondary streams, it is unlikely that they contribute more than 20 to 40% of the river flux. An estimate for the freshwater input of Mn from these streams and waterfalls is 40 kmol yr^{-1}. This results in a total freshwater input of Mn to Smeaton Bay of 164 kmol yr^{-1}.

The apparent "excess" Mn is highly sensitive to the diffusive fluxes of Mn calculated from the interstitial water profiles. As shown in Chapter 4, the distribution of reactive solutes in the pore waters of Smeaton Bay is highly time-dependent. In the above mass balance calculations, I use interstitial water profiles and

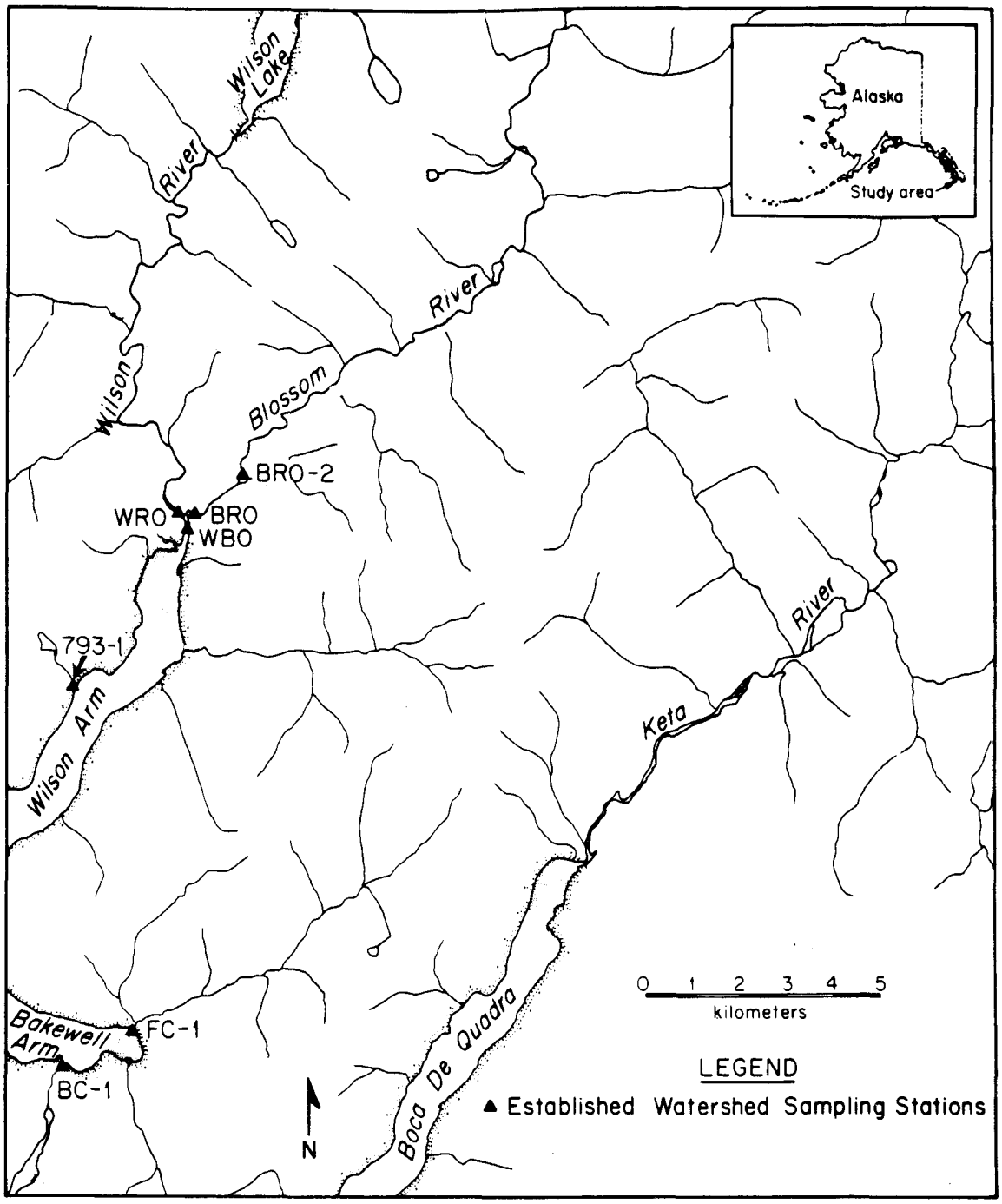

Fig. 1. Location of stations in study area.

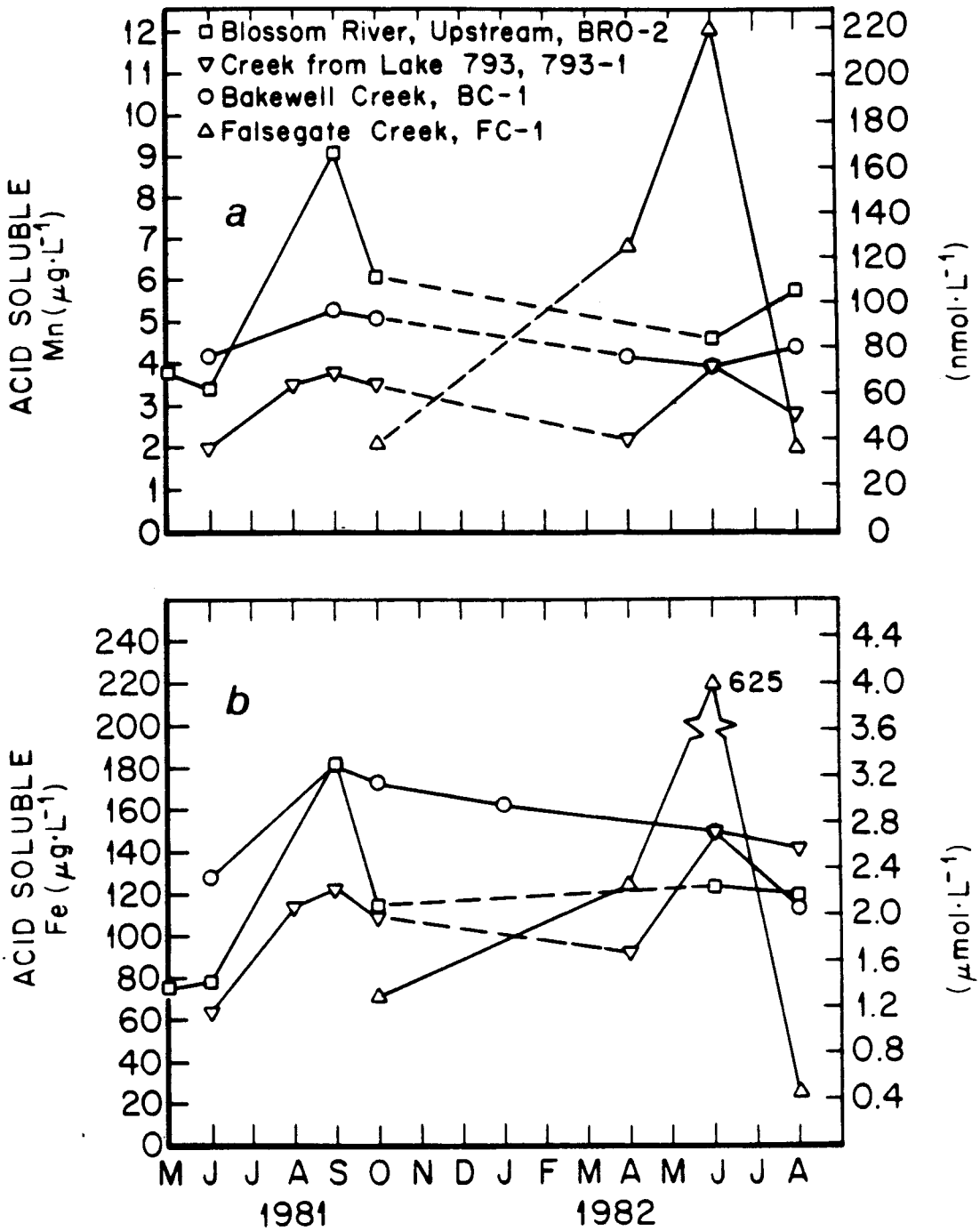

Fig. 2. a. Acid-soluble Mn vs. time for watershed stations.
b. Acid-soluble Fe vs. time

sedimentation rates determined on cores from August-September 1982. By doing this, I likely overestimate the sediment flux. As shown in Table 1 of Chapter 4, the estimated diffusive fluxes calculated at the basin station, SB1, vary by as much as 60%, and the flux estimated from the August 1982 core is relatively high. A decrease in the sediment flux by approximately 40% removes the "excess" Mn input for Smeaton Bay. However, the calculated Mn flux from the sediments in the deep basin of Boca de Quadra is 1740 kmol yr^{-1}, or more than 10 times that supplied by the Wilson-Blossom River to Smeaton Bay. The combined Marten-Red River flow is approximately equal to that of the Wilson-Blossom River, indicating that a much greater apparent "excess" of Mn is supplied to the central basin of Boca de Quadra from sediment remobilization. Without water column measurements, it is impossible to estimate the quantity of Mn mobilized from the sediments that is recycling within the deep waters of the fjords. In this deep basin of Boca de Quadra, where mixing is infrequent and solid phase as well as interstitial Mn is greatly enhanced in the surficial sediment, reprecipitation of the solubilized Mn is likely. Thus, on the basis of my freshwater and sediment determinations in Smeaton Bay and Boca de Quadra, I suggest that the fjord sediments are the most important input term to a fjord mass balance of Mn. This is in contrast to Robb (1981), who based upon observations of the water column, particulate matter, and sediment near the head of Boca de Quadra, concluded that the Keta River rather than sediment remobilization was the dominate source of Mn. As shown in Table 2, the sediment fluxes of Mn are

lowest in the inner basin of Boca de Quadra, suggesting that the relative importance of river input would be greater there. Thus, on a total fjord basis, I speculate that the sediments are the major source of Mn to the water column inside, and, perhaps, outside the entrance sill.

THESIS SUMMARY

Close interval sampling of the watershed and sediments of two pristine, non-glacial fjords in southeast Alaska has shown that:

(1) Because of extremely high precipitation and watersheds limited by high relief, river concentrations and exports of phosphate, ammonia, and Cu are low for most of the year. The maximum nutrient export from the Wilson-Blossom River system appears to be closely tied to the annual salmon cycle while Cu concentrations are flow dependent.

(2) Iron and Mn export rates from the watersheds are much higher than those for Cu, reflecting solubilization of Fe and Mn under reducing conditions that develop in muskeg ponds during drought periods. The association of metals with organics allows transport of Fe and possibly other metals throughtout the fjord system, in contrast with the large-scale removal of metals in or near the river's mouth, observed elsewhere.

(3) River exports of carbon and trace metals are predominately in the dissolved rather than particulate form. The ratio of DOC:POC for the Wilson-Blossom Rivers is generally in the range of 10 to 30.

(4) Sedimentation in Smeaton Bay and Boca de Quadra is characterized by frequent physical mixing and episodic slumping. In

the basins of the fjords, where sediment focusing and less mixing occur, the ^{210}Pb sedimentation rates are 88 $\pm$ 15 mg $cm^{-2}yr^{-1}$ and reducing conditions exist near the sediment-water interface. Sedimentation rates in the shallower regions closer to river influence are 68 $\pm$ 39 mg $cm^{-2}yr^{-1}$ with mixing coefficients ranging from >6.6 to >65 $cm^{2}yr^{-1}$ responsible for the observed surface mixed layer. ^{137}Cs inventories suggest that terrestial material is about twice as important to the total sediment accumulation in Wilson Arm and Marten Arm than in Smeaton Bay or Boca de Quadra.

(5) Temporal variations in interstitial water profiles from shallow and basin stations in Smeaton Bay indicate that episodic physical mixing and the supply of reactive organic matter control the flux of reactive solutes. Because of frequent mixing in Smeaton Bay, thermodynamic controls on Mn, Fe, and phosphate concentrations are not observed. In contrast, reducing conditions in sediments from the main basin of Boca de Quadra result in large fluxes of Mn^{2+}, which appear to be in equilibrium with rhodochrosite or similar Mn carbonate.

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Appendix E. Additional watershed and interstitial water data used in mass balance calculations.

a) Discharge data for Falsegate Creek at Bakewell Arm (VTN, unpublished data).

Date	Discharge (cfs)
9-27-78	31.2
5- 2-79	250
8- 8-79	62
11- 8-79	17.4
2-22-80	26.2
5-15-80	97
8-20-80	65
11-21-80	139

b) Manganese concentrations in Falsegate Creek at Bakewell Arm.

Date	Acid-soluble manganese ug L^{-1}
6-14-81	0.2
10-18-81	2.1
4-12-82	6.8
6- 5-82	12.1
8-28-82	2.0

c) Diffusive flux calculations for Boca de Quadra inner basin.

Station BQ3	Station BQ3A
c_1 = 17.7 umol L^{-1}	c_1 = 5.39 umol L^{-1}
z = 1.15 cm	z = 1.25 cm